

Simple Construction of Energy-Resolved Wannier States with Assigned Local Symmetry

Application to quasi-1D Cu-O spin chains

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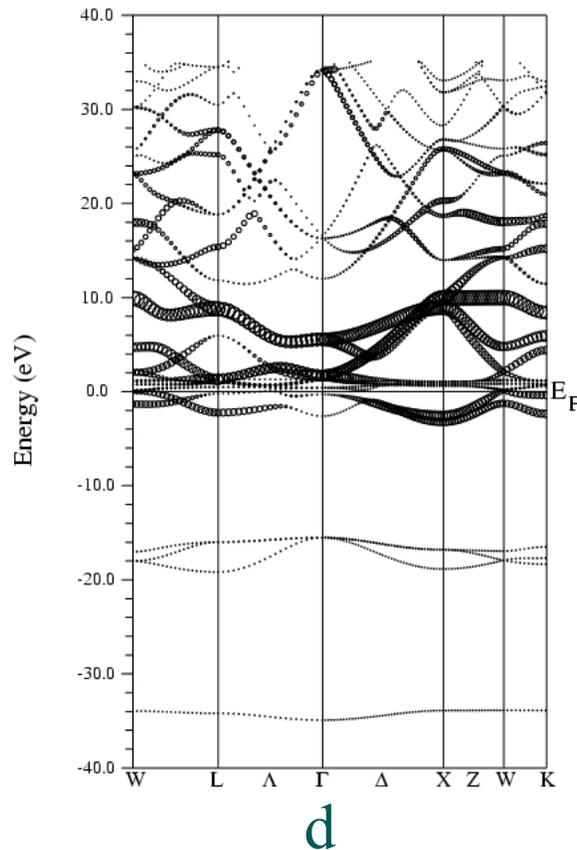
Desired Properties of Wannier Representation

- Local representation
 - ideal for strongly correlated states
- Energy resolution ¹
 - minimal, simplest basis for low energy physics
 - non-perturbative inclusion of hybridization
 - narrow energy spectrum, good for RG and MBPT
- Orthonormal ¹
 - well-defined basis for 2nd quantization
- Local symmetry respecting ²
 - simpler analysis
 - increased sparseness in hoppings
- Flexible bias for better control ¹²³
- Simple, efficient procedure of construction (avoid $\langle \mathbf{k} j | e^{-i\mathbf{q}\hat{\mathbf{x}}} | \mathbf{k} + \mathbf{q} j' \rangle$ or iterations) ¹²
- General procedure independent of underlying representation ³

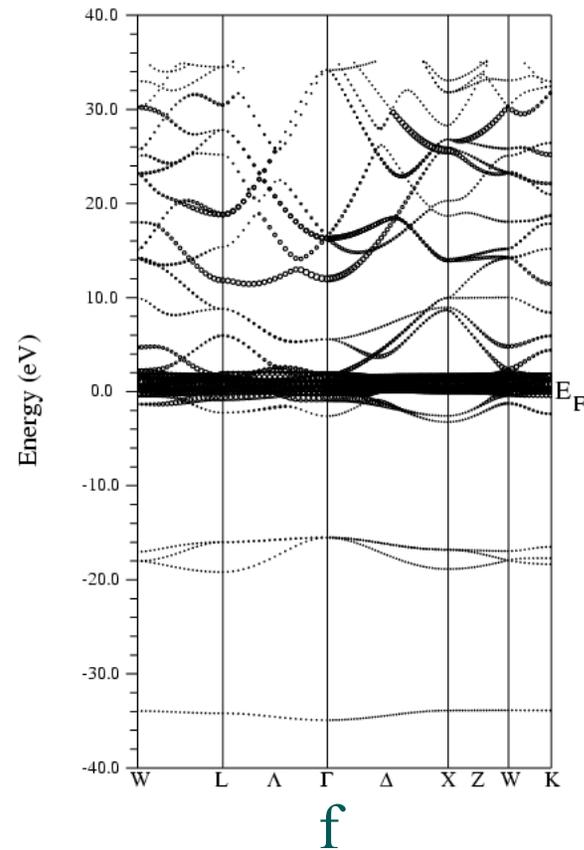
1. not with atomic representation
2. not with MaxLoc construction
3. not with “down-folding” of NMTO

Our Strategy:

- Information from Bloch states and their eigenvalues
- Multiple-energy windows
- Maximized contribution in specified local symmetry
- Specified bias for better control



Ce



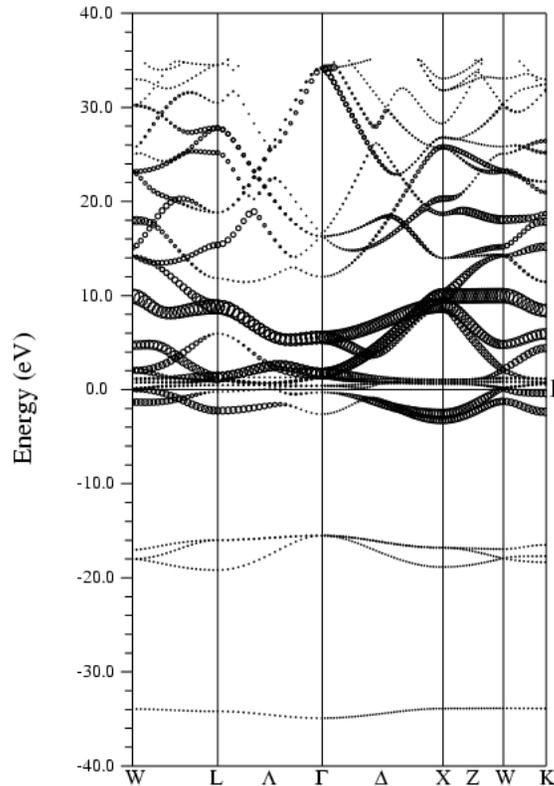
Definition of Wannier States

$$|Rn\rangle \equiv |\bar{k}n\rangle e^{-i\bar{k}\cdot R} / \sqrt{\#}$$

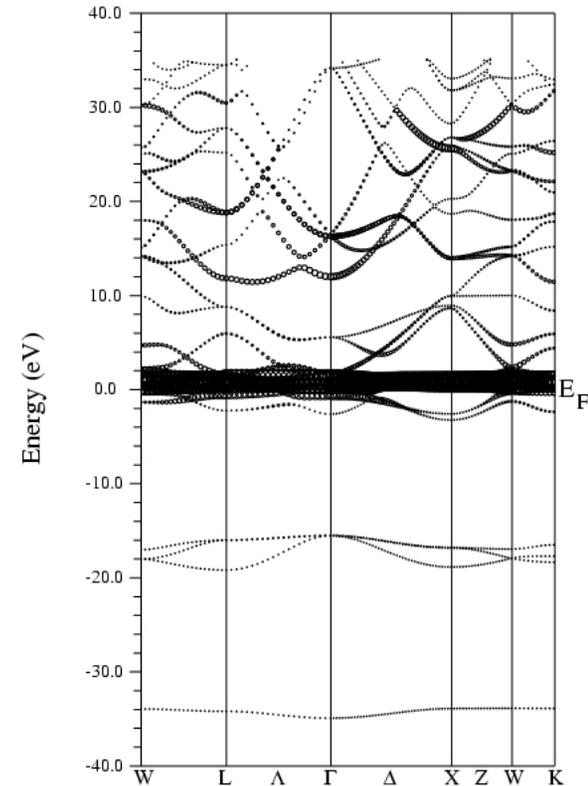
$$|kn\rangle = |\phi_{k\bar{m}}\rangle \langle \phi_{k\bar{m}} | kn \rangle$$

$$\langle \phi_{km} | kn \rangle = \langle \phi_{km} | g_{\bar{n}'} \rangle M_{\bar{n}'n}$$

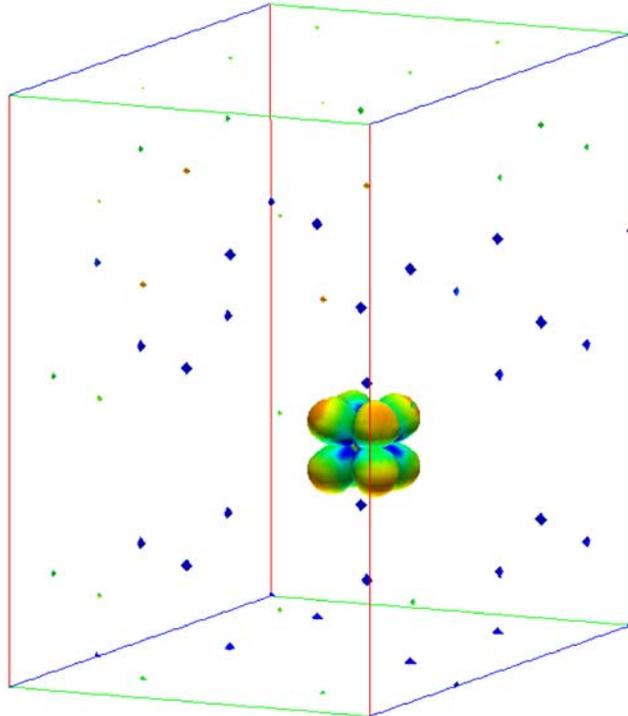
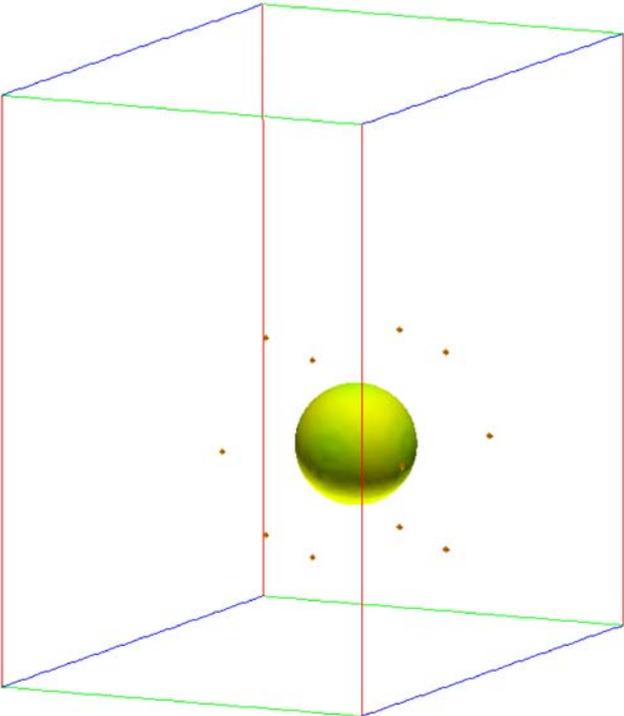
$$M_{n'n}^{-2} \equiv \langle g_{n'} | \phi_{k\bar{m}} \rangle \langle \phi_{k\bar{m}} | g_n \rangle$$



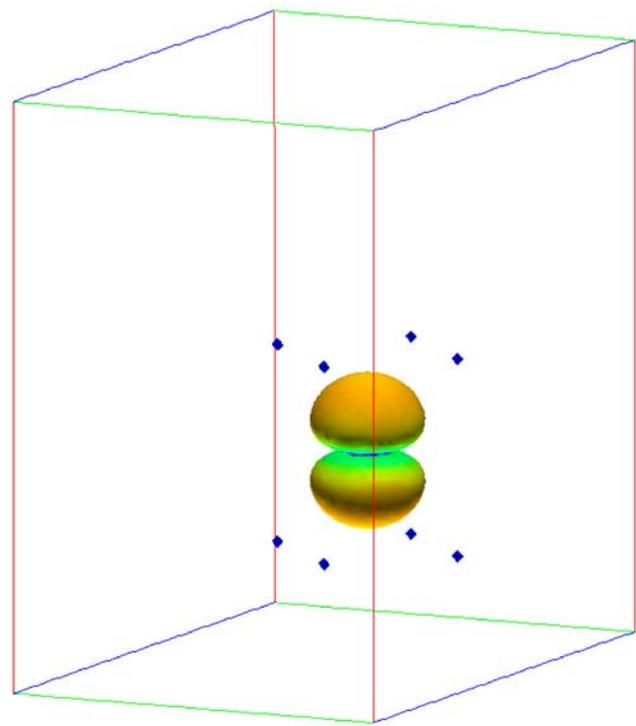
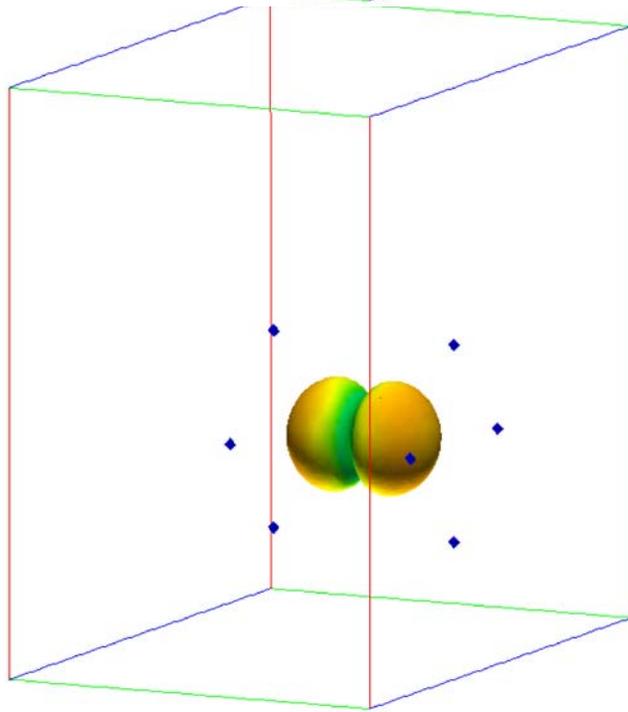
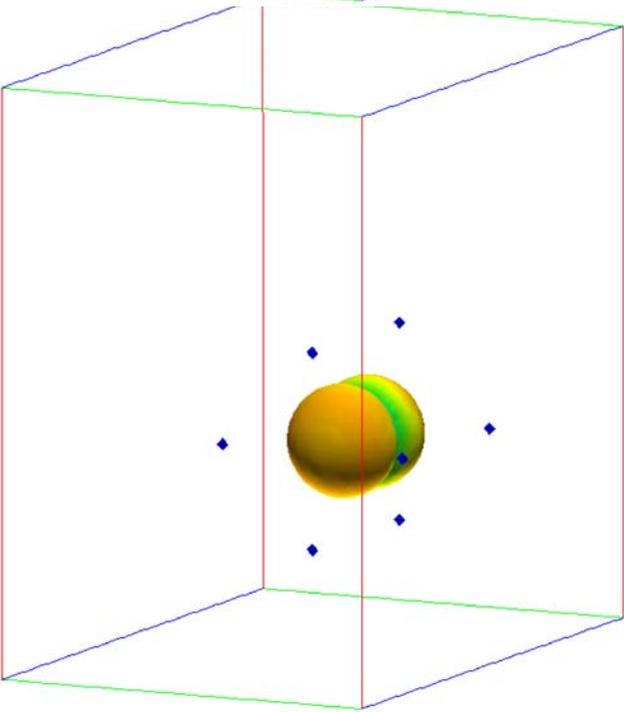
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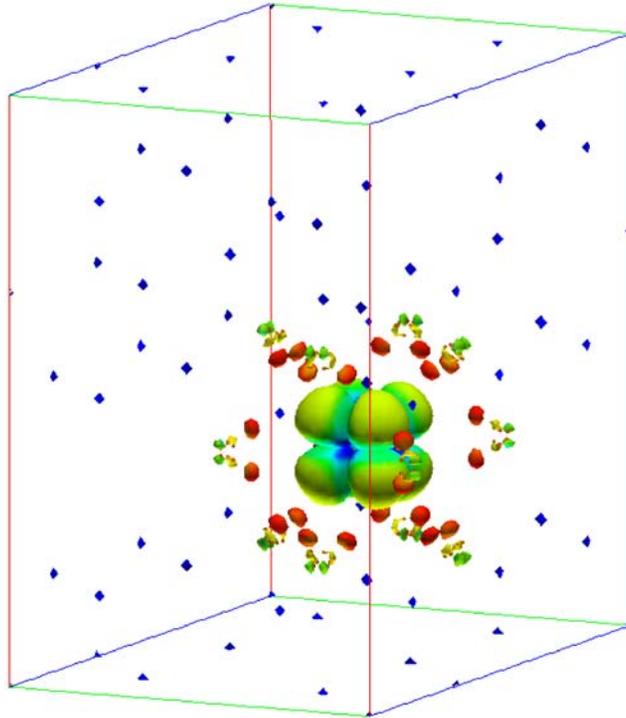
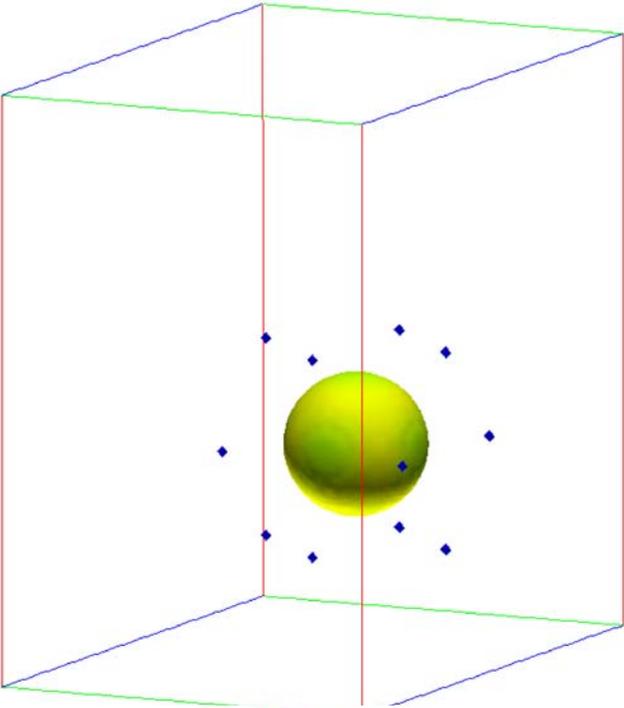


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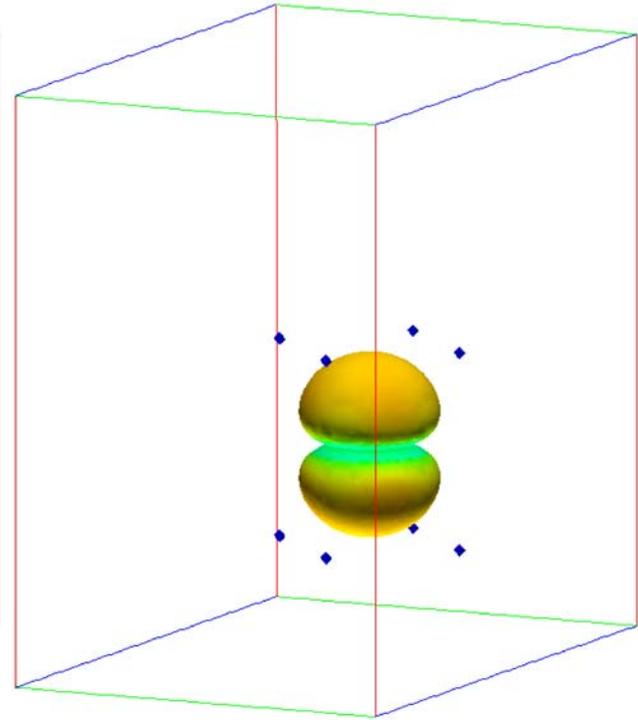
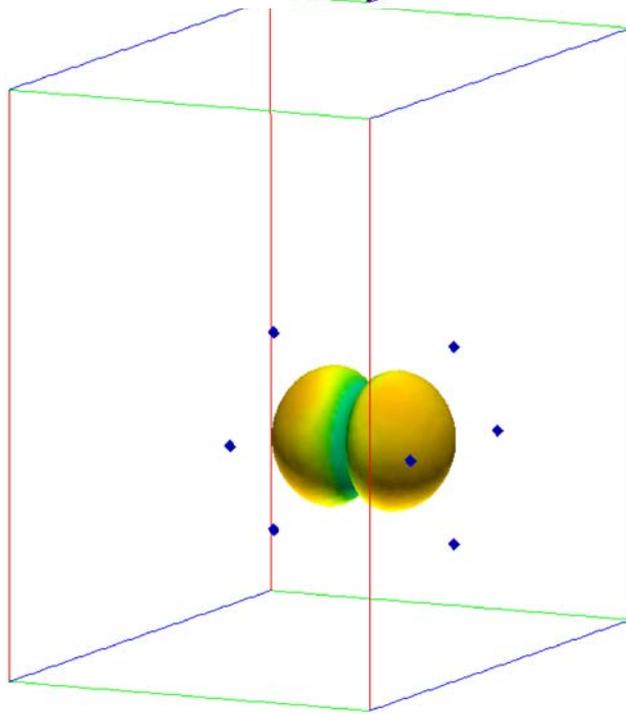
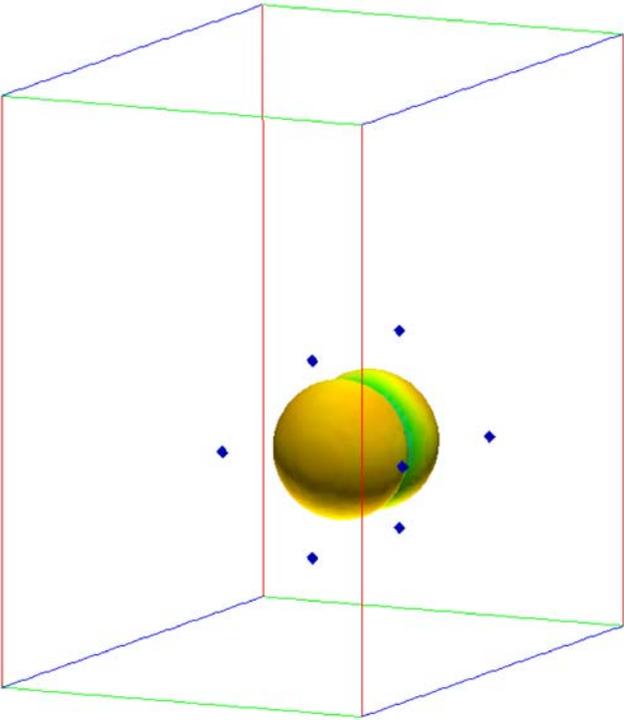


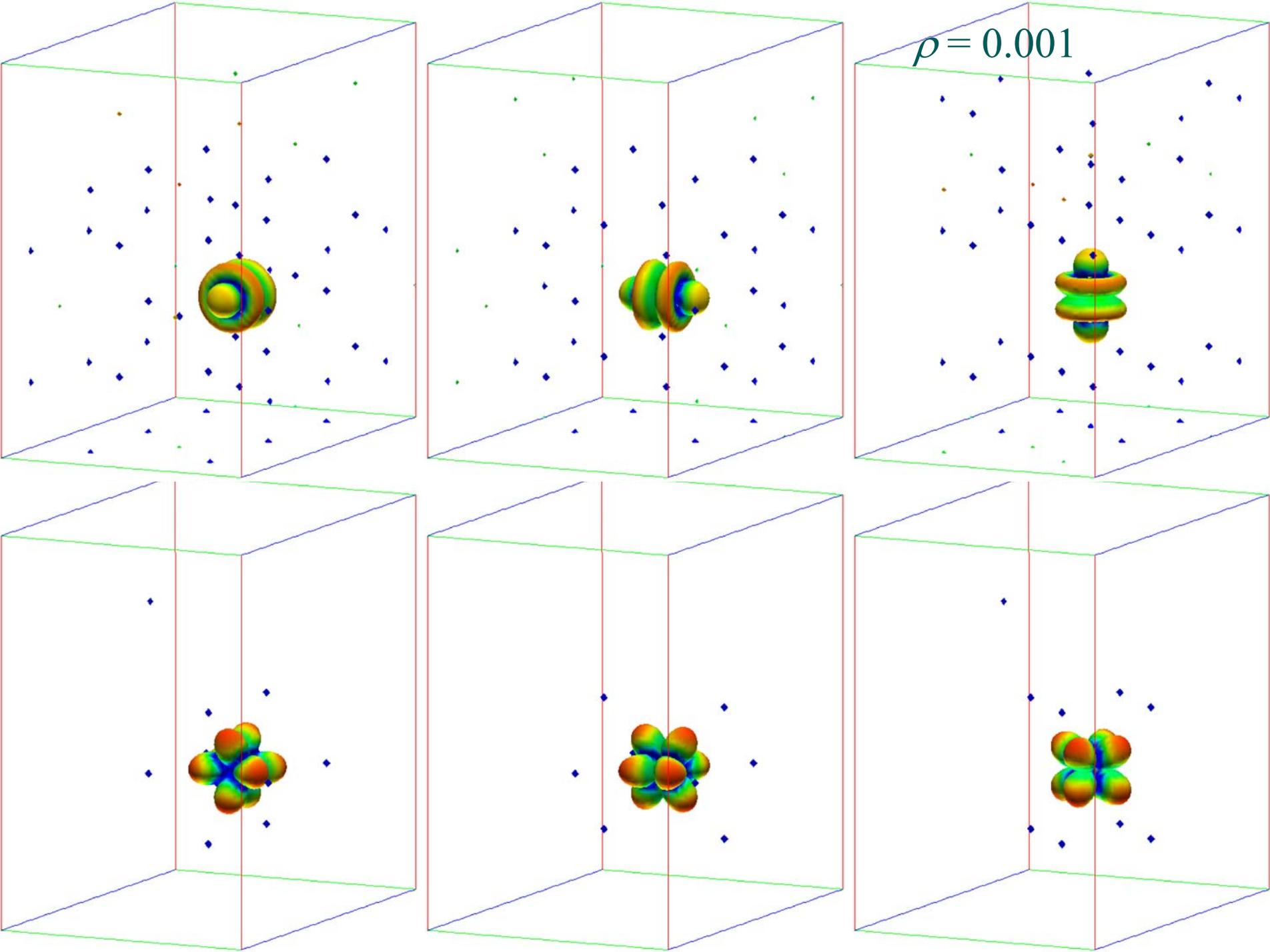
$\rho = 0.001$

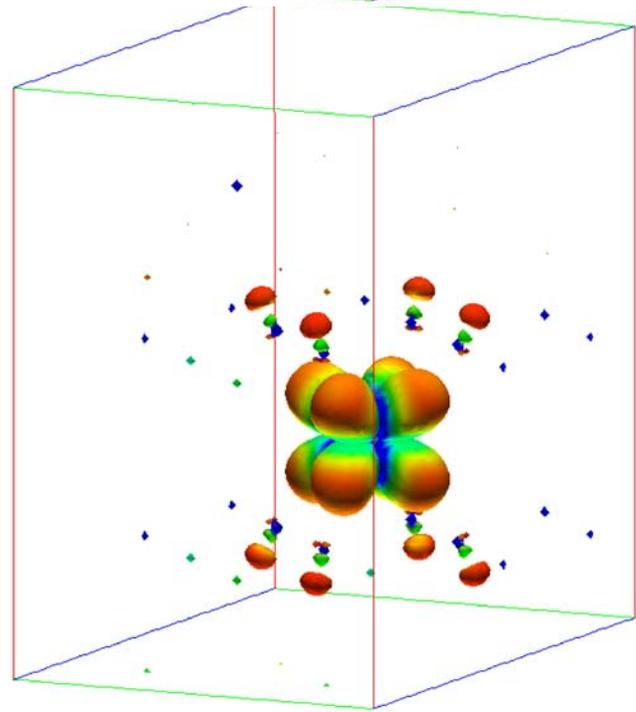
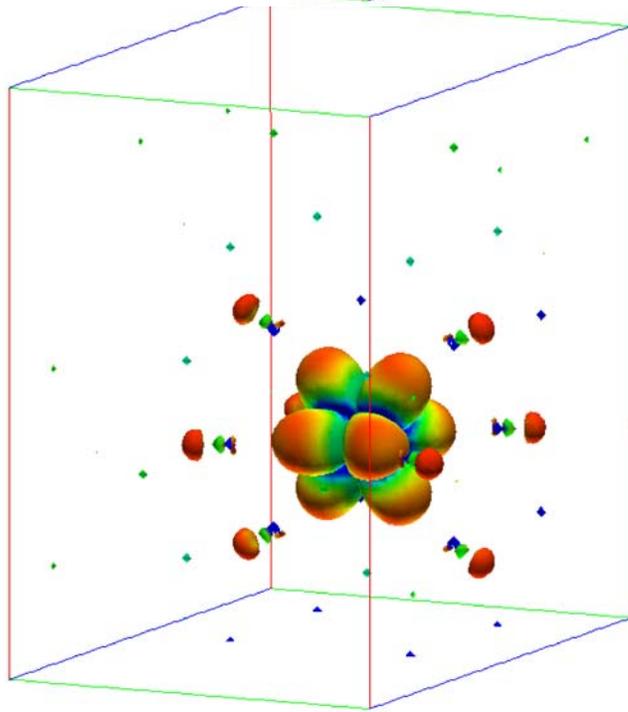
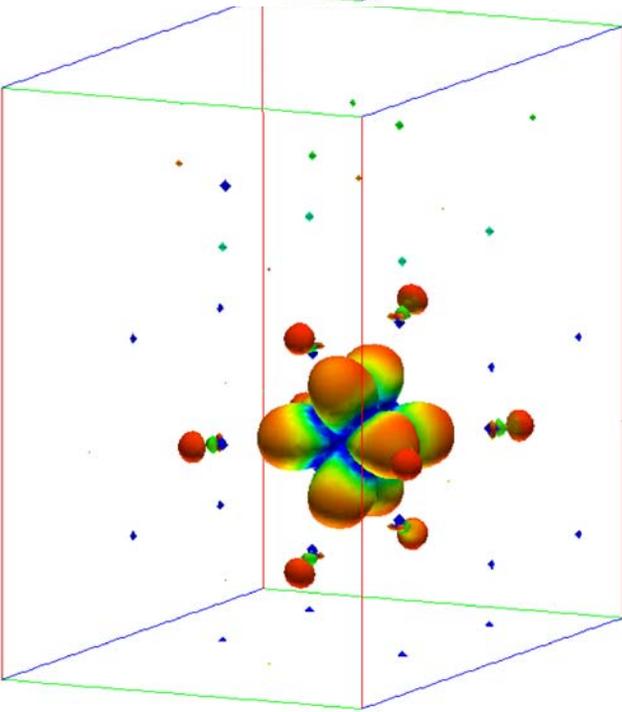
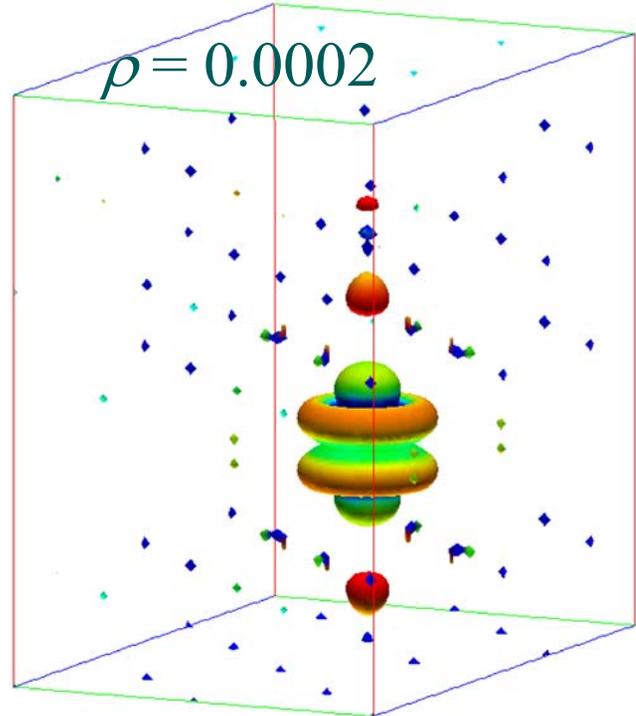
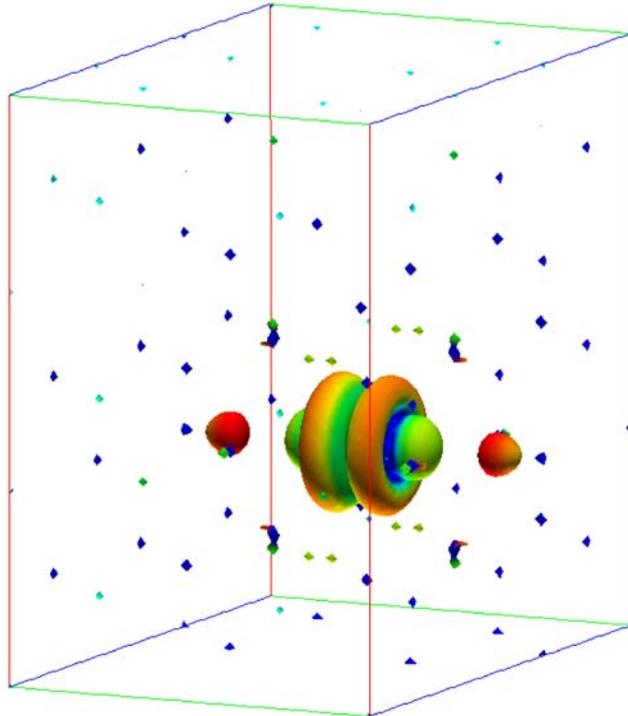
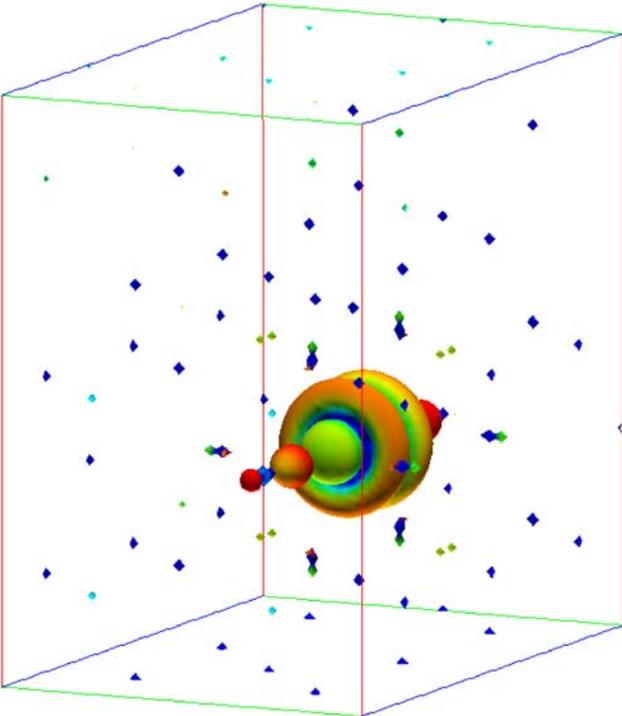


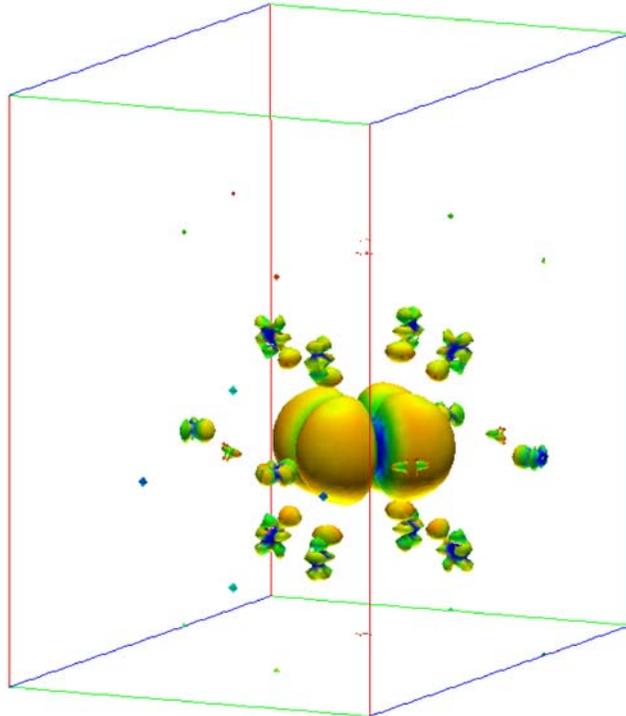
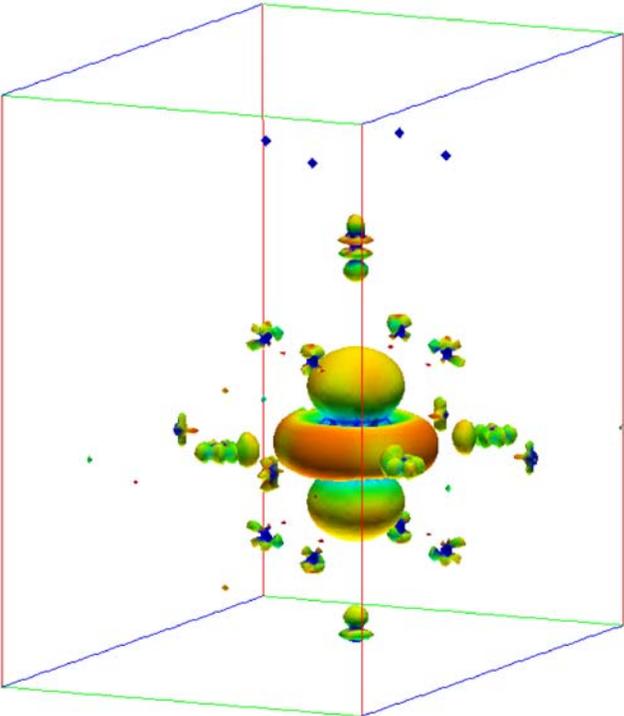


$$\rho = 0.0002$$

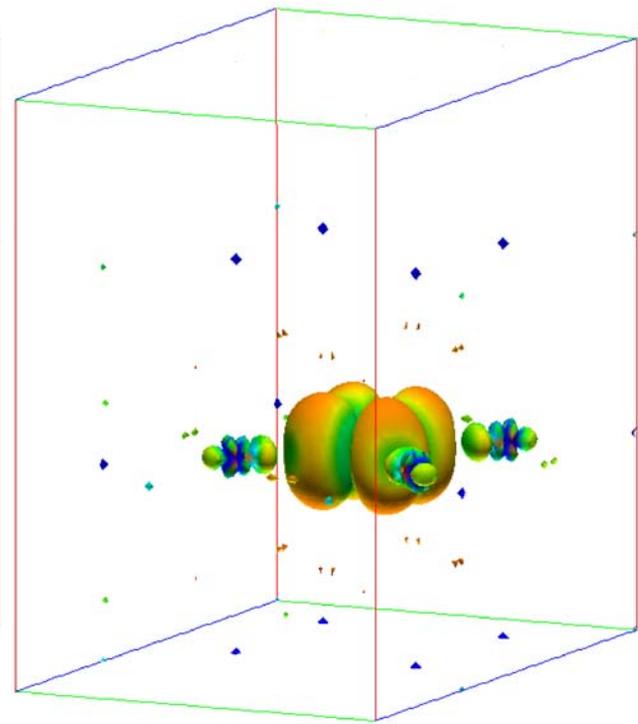
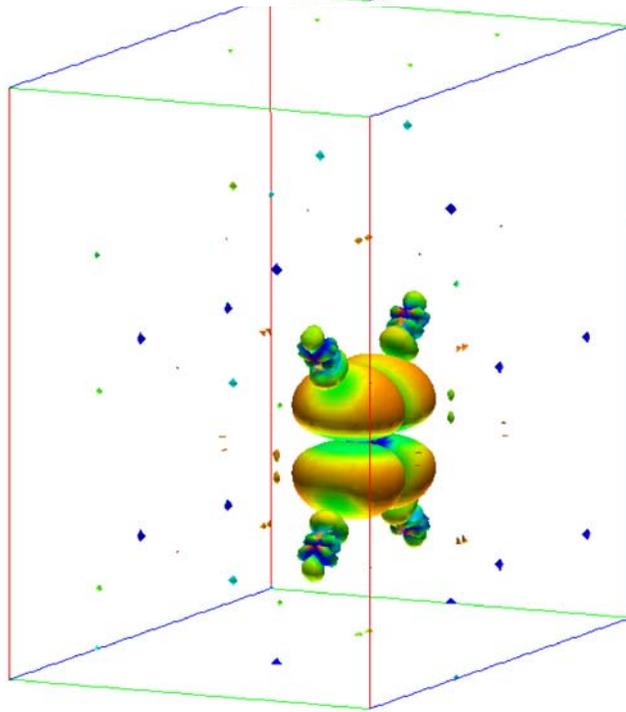
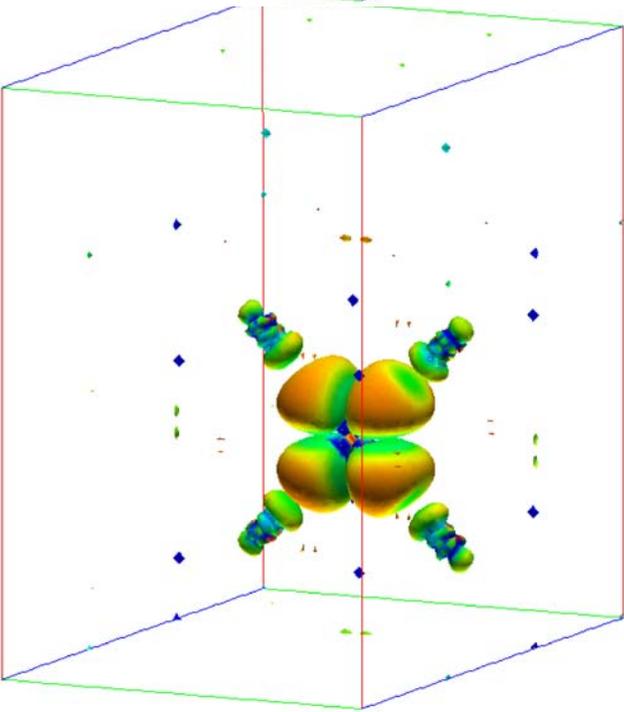


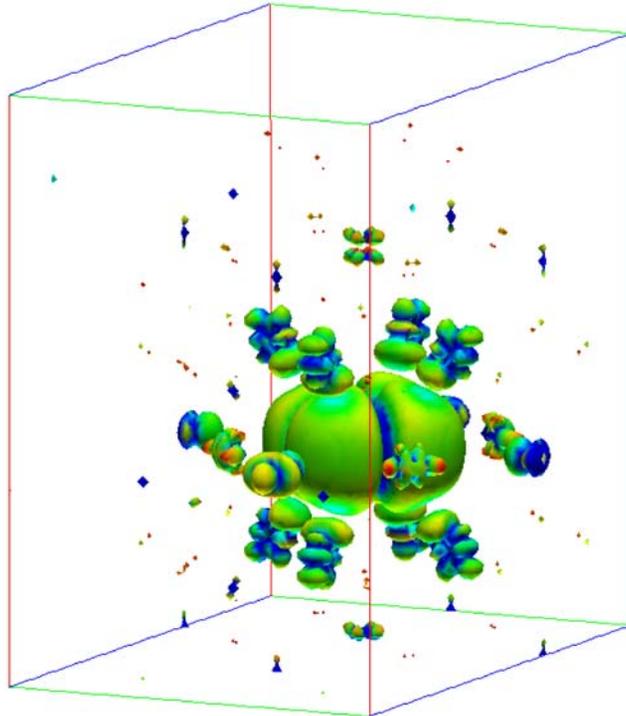
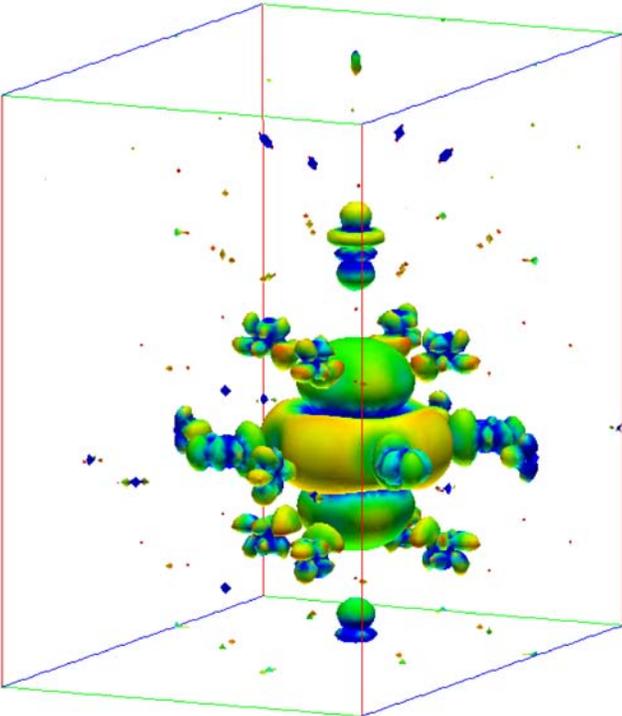




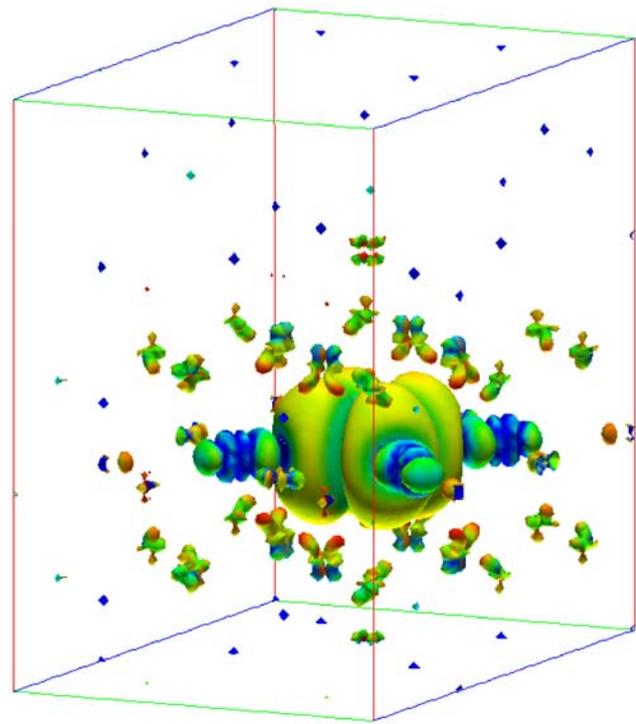
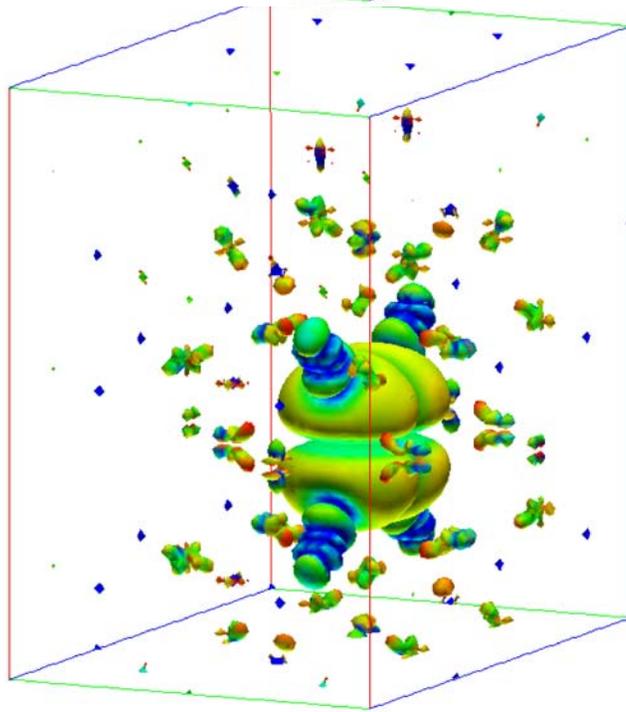
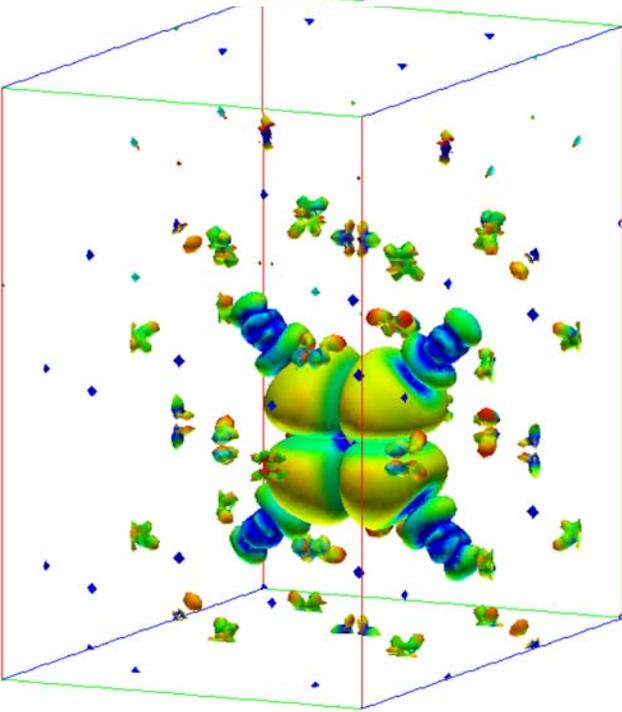


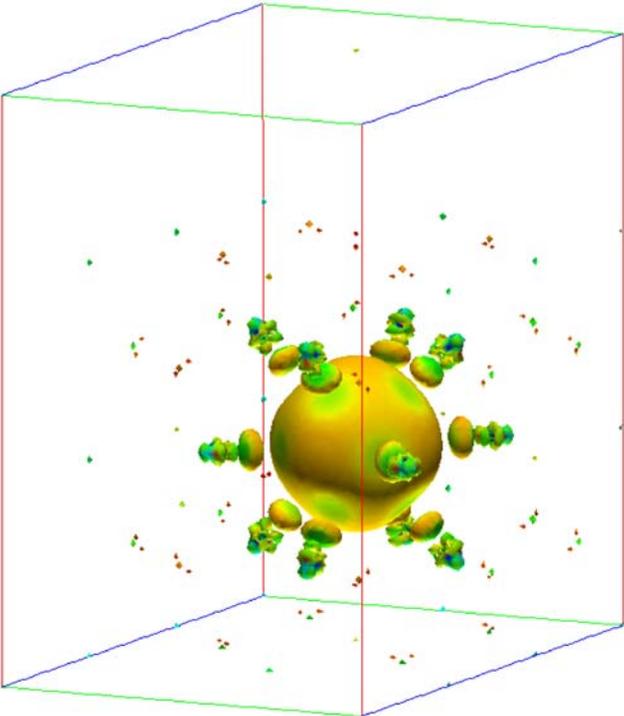
$\rho = 0.001$



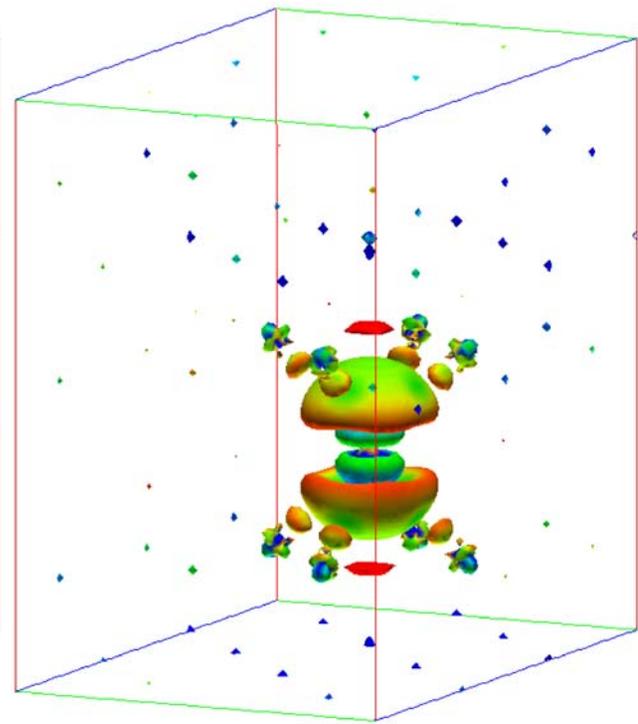
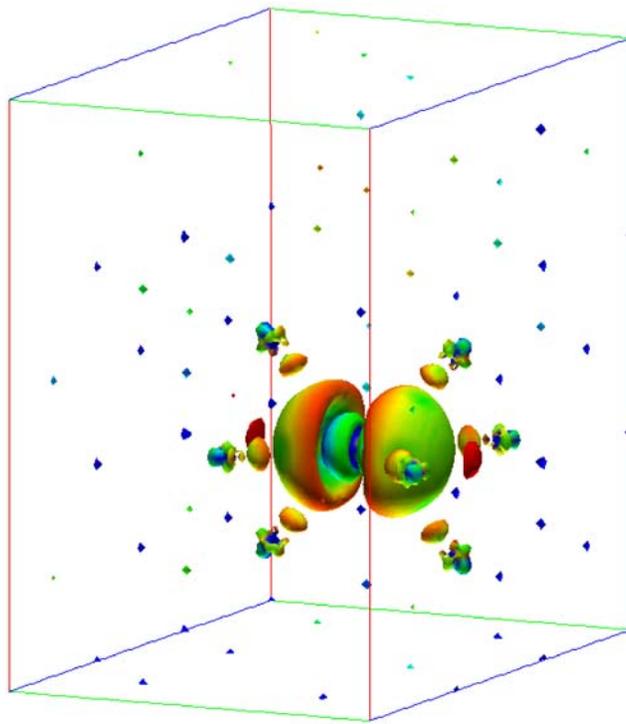
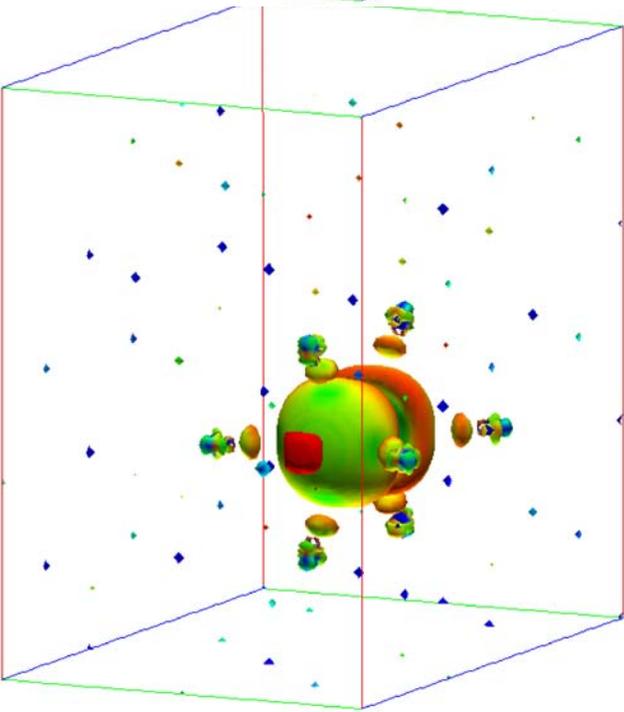


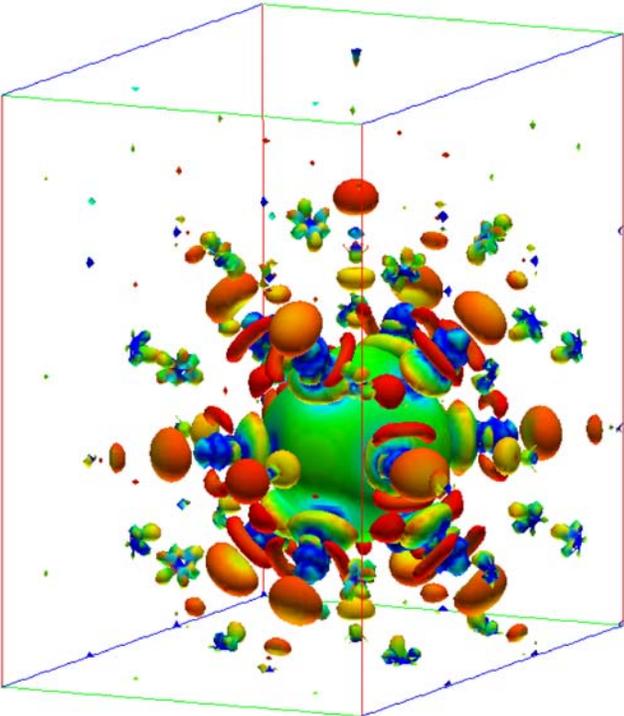
$$\rho = 0.0002$$



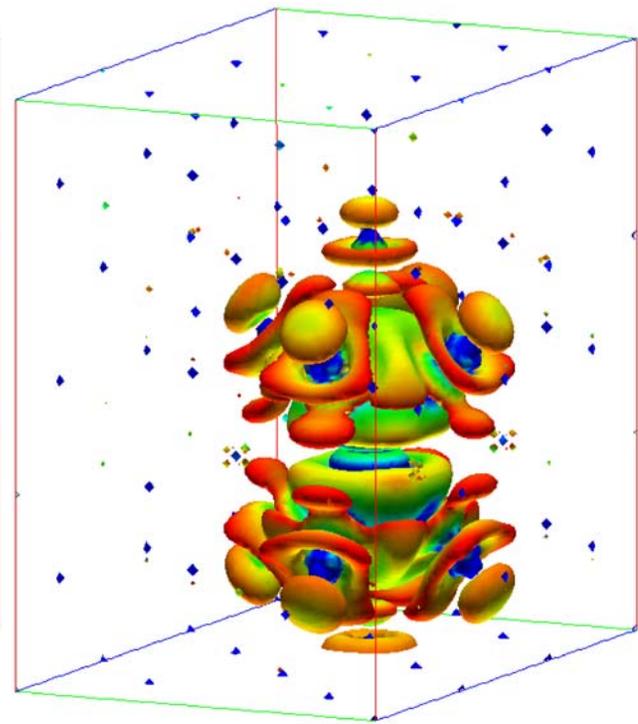
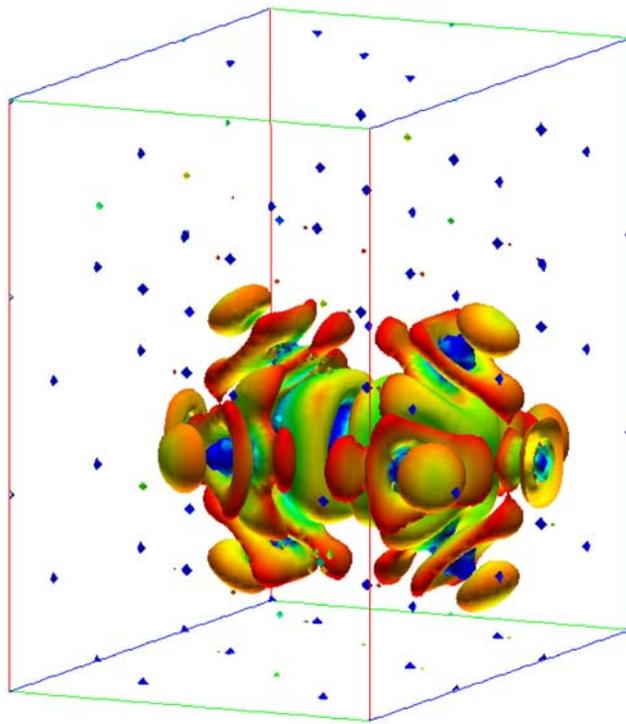
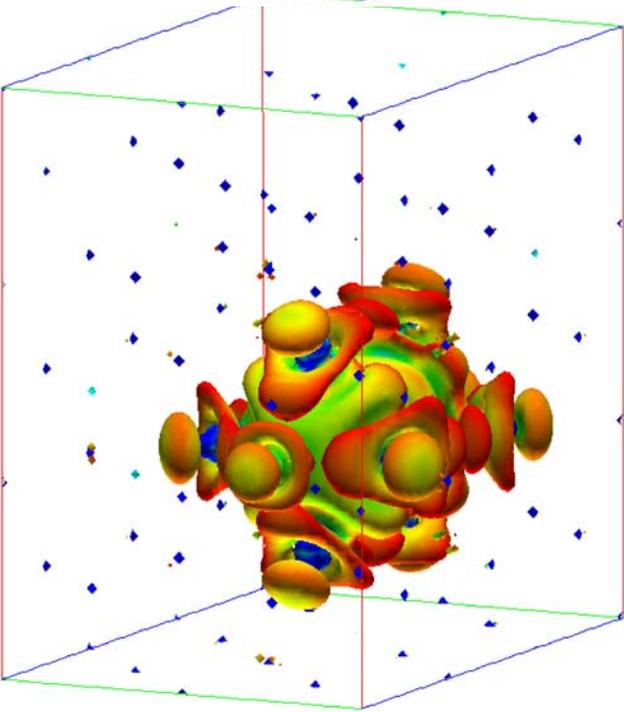


$$\rho = 0.001$$





$$\rho = 0.0002$$



Tight-Binding Parameters

$\langle R j' | h^{DFT} | 0 j \rangle$ of γ -Ce (eV)

occupation #	2	2	2	2	0.159	0.148	0.148	0.148	0.039	0.039	0.039	0.540	0.540	0.565	0.565	0.565	0.344		
(0 0 0) s	s -34.216	p x	p y	p z	f xyz	f x(5x2-3r2)	f y(5y2-3r2)	f z(5z2-3r2)	f x(y2-z2)	f y(z2-x2)	f z(x2-y2)	d 3z2-r2	d x2-y2	d yz	d zx	d xy	s	(0 0 0) s	
p x		-17.143																p x	
p y			-17.143															p y	
p z				-17.143														p z	
f xyz					0.885													f xyz	
f x(5x2-3r2)						0.795												f x(5x2-3r2)	
f y(5y2-3r2)							0.795											f y(5y2-3r2)	
f z(5z2-3r2)								0.795										f z(5z2-3r2)	
f x(y2-z2)									0.619									f x(y2-z2)	
f y(z2-x2)										0.619								f y(z2-x2)	
f z(x2-y2)											0.619							f z(x2-y2)	
d 3z2-r2												3.570						d 3z2-r2	
d x2-y2													3.570					d x2-y2	
d yz														3.592				d yz	
d zx															3.592			d zx	
d xy																3.592		d xy	
s																	9.614	s	
(0 1 1) / 2 s	s -0.064	p x	p y	p z	f xyz	f x(5x2-3r2)	f y(5y2-3r2)	f z(5z2-3r2)	f x(y2-z2)	f y(z2-x2)	f z(x2-y2)	d 3z2-r2	d x2-y2	d yz	d zx	d xy	s	(0 1 1) / 2 s	
p x		-0.047																p x	
p y			0.215	0.273														p y	
p z			0.273	0.215														p z	
f xyz					-0.023	0.038											-0.029	-0.029	f xyz
f x(5x2-3r2)					0.038	-0.081											0.020	0.020	f x(5x2-3r2)
f y(5y2-3r2)							-0.044	0.030		0.018	0.029	0.022	0.009	-0.016				-0.004	f y(5y2-3r2)
f z(5z2-3r2)							0.030	-0.044		-0.029	-0.018	-0.018	-0.015	-0.016				-0.004	f z(5z2-3r2)
f x(y2-z2)									0.036						0.004	-0.004			f x(y2-z2)
f y(z2-x2)										0.036	-0.047	-0.002	-0.004	0.011				-0.004	f y(z2-x2)
f z(x2-y2)											0.036	-0.005	-0.004	-0.011				0.004	f z(x2-y2)
a 3z2-r2												0.578	0.607	-0.428				0.116	a 3z2-r2
a x2-y2												0.607	-0.124	0.742				-0.200	a x2-y2
d yz												-0.428	0.742	-1.247				0.369	d yz
d zx					0.029	-0.020			-0.004						0.348	0.632			d zx
d xy					0.029	-0.020			0.004						0.632	0.348			d xy
s							0.004	0.004		0.004	-0.004	0.116	-0.200	0.369				-1.197	s
s	s	p x	p y	p z	f xyz	f x(5x2-3r2)	f y(5y2-3r2)	f z(5z2-3r2)	f x(y2-z2)	f y(z2-x2)	f z(x2-y2)	d 3z2-r2	d x2-y2	d yz	d zx	d xy	s		

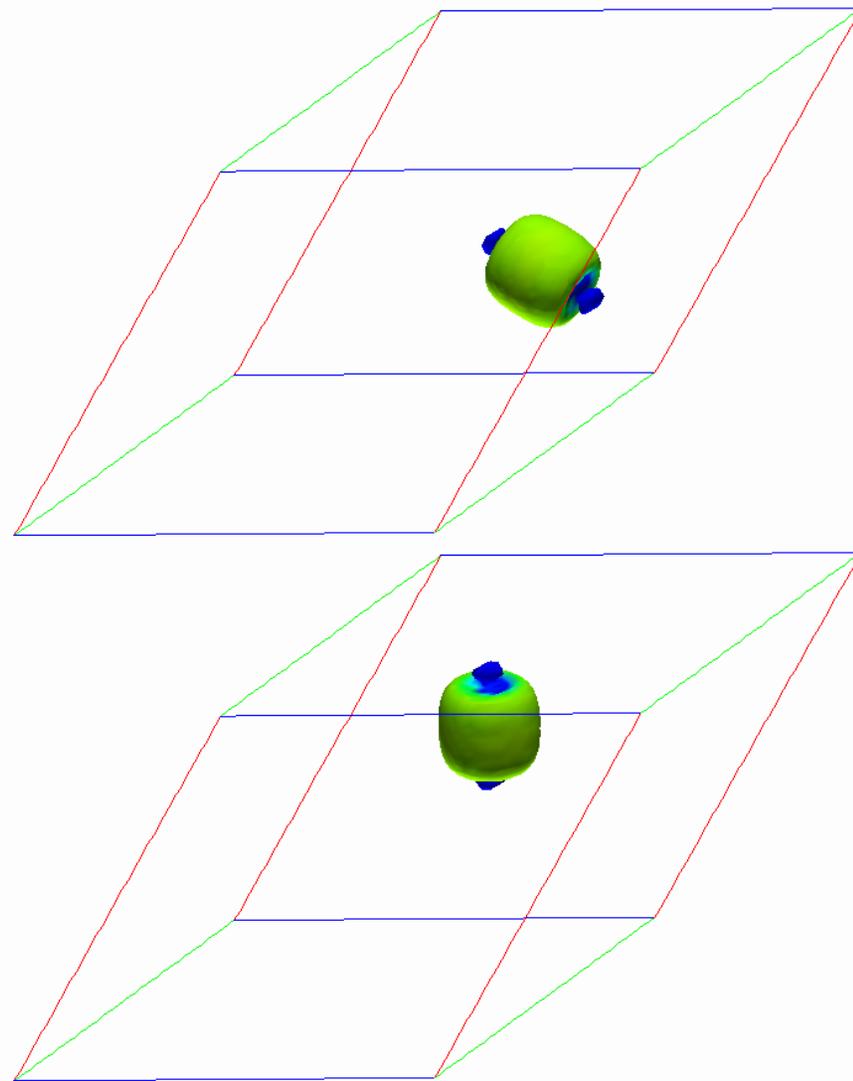
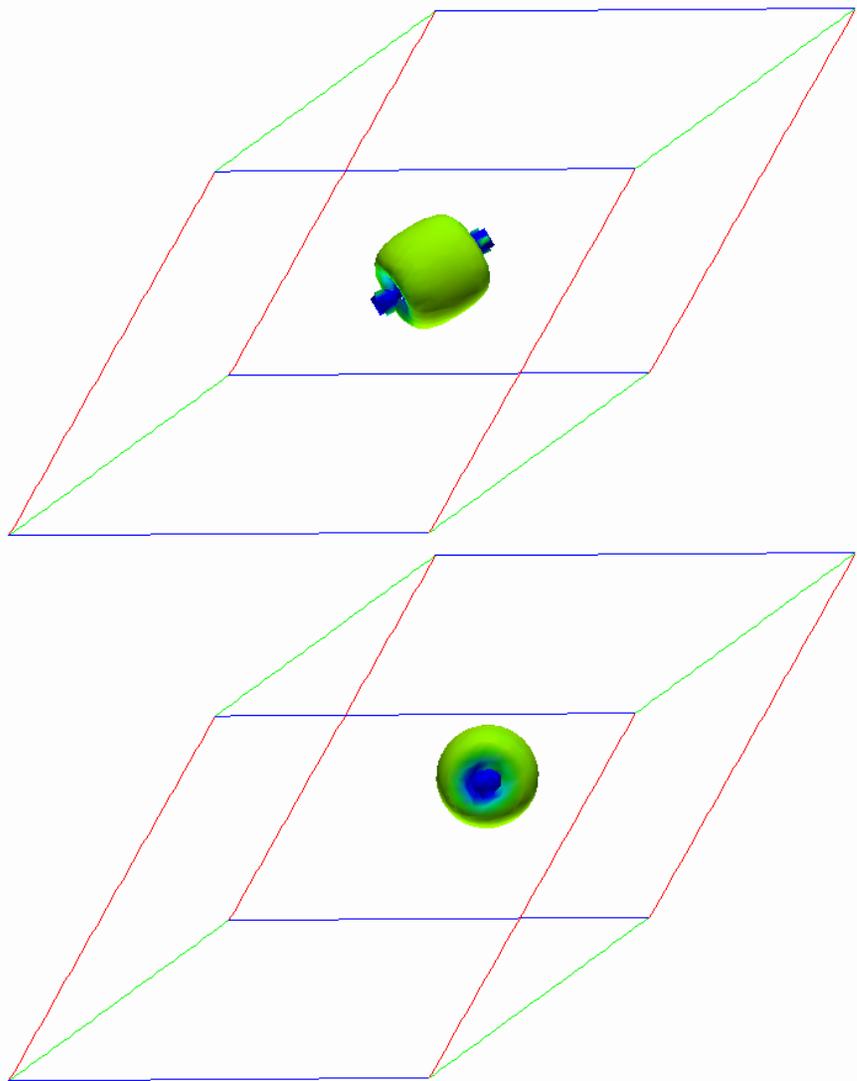
sparser than atomic tight-binding parameters !

Tight-Binding Parameters

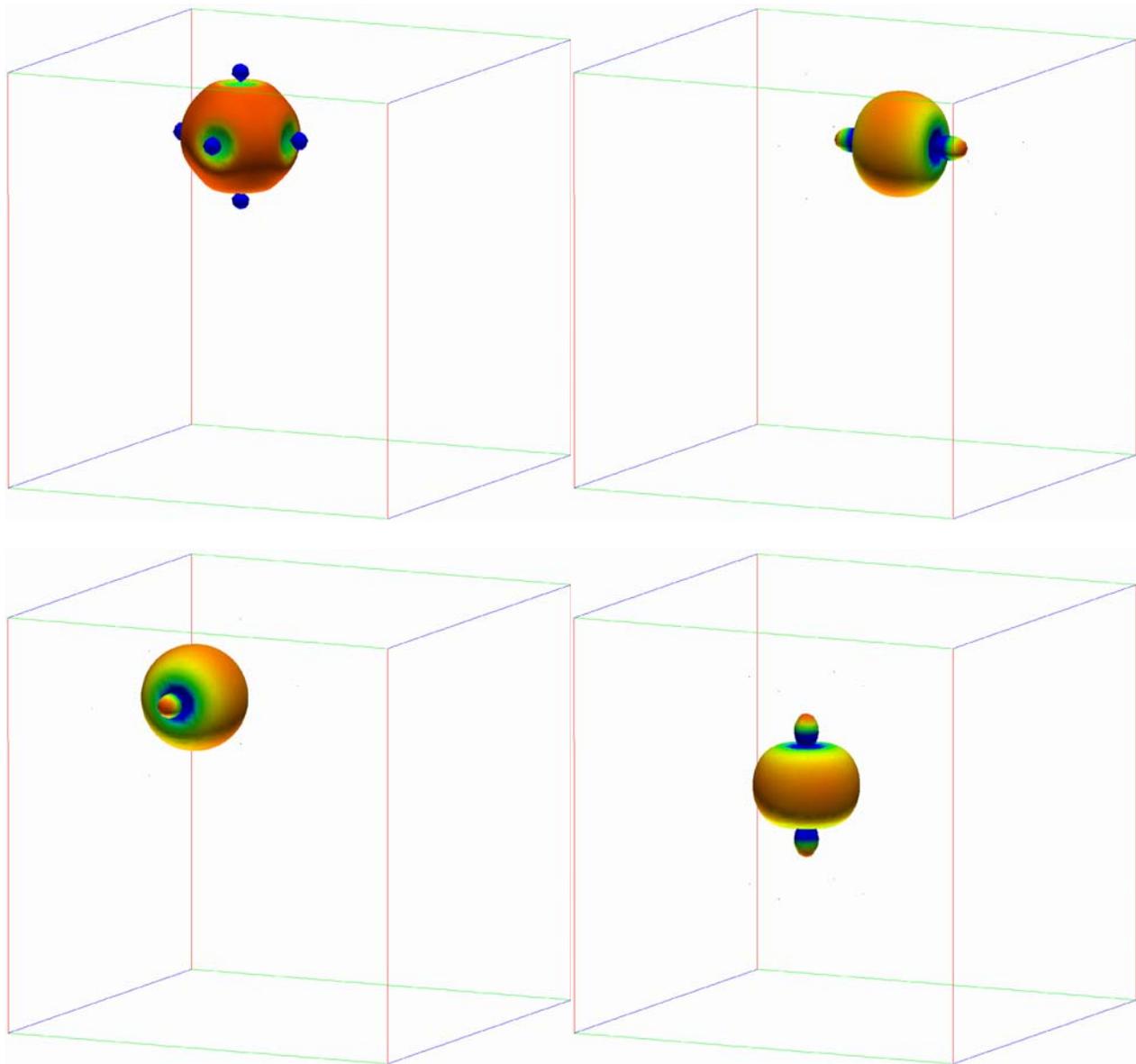
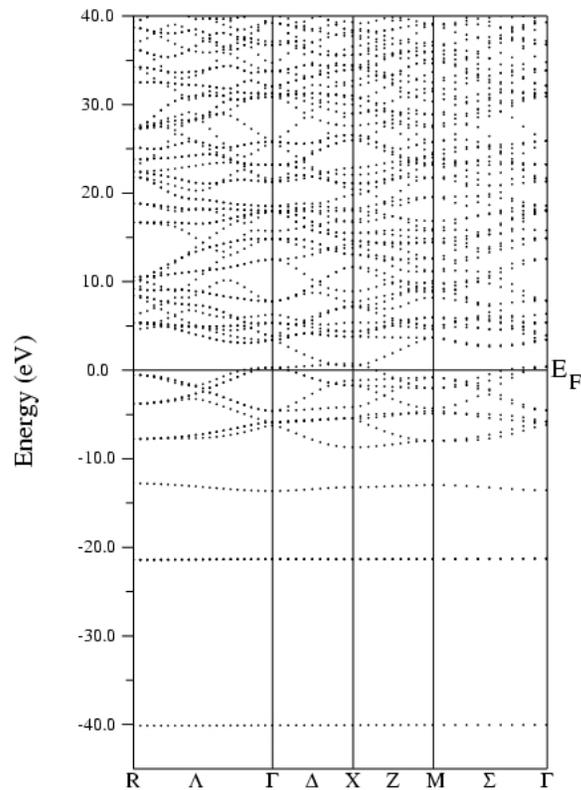
(1 0 0)	s	p x	p y	p z	f xyz	f x(5x2-3r2)	f y(5y2-3r2)	f z(5z2-3r2)	f x(y2-z2)	f y(z2-x2)	f z(x2-y2)	d 3z2-r2	d x2-y2	d yz	d zx	d xy	s	(1 0 0)
s																		s
p x		0.003																p x
p y			0.001															p y
p z				0.001														p z
f xyz					0.031									-0.015				f xyz
f x(5x2-3r2)						-0.023						-0.010	0.017				-0.003	f x(5x2-3r2)
f y(5y2-3r2)							-0.004										0.009	f y(5y2-3r2)
f z(5z2-3r2)								-0.004									0.009	f z(5z2-3r2)
f x(y2-z2)									-0.002				-0.001					f x(y2-z2)
f y(z2-x2)										-0.009								f y(z2-x2)
f z(x2-y2)											0.011							f z(x2-y2)
a 3zz-r4								0.010										a 3zz-r4
a xz-y4								-0.017										a xz-y4
d yz						0.015												d yz
d zx														0.145				d zx
d xy															0.013			d xy
s																		s
(2 1 1) / 2	s	p x	p y	p z	f xyz	f x(5x2-3r2)	f y(5y2-3r2)	f z(5z2-3r2)	f x(y2-z2)	f y(z2-x2)	f z(x2-y2)	d 3z2-r2	d x2-y2	d yz	d zx	d xy	s	(2 1 1) / 2
s																		s
p x		0.001																p x
p y			0.001															p y
p z				0.004														p z
f xyz																		f xyz
f x(5x2-3r2)					-0.024	0.001		-0.005	-0.005		0.001	-0.001	0.001	-0.001	0.001	0.001	-0.006	f x(5x2-3r2)
f y(5y2-3r2)					0.001	0.012		0.015	0.015		0.006	-0.006	-0.002	0.004	-0.004	-0.001	-0.001	f y(5y2-3r2)
f z(5z2-3r2)					-0.005	0.015		0.003	-0.011	0.013	-0.005	-0.001	-0.011		0.004	-0.002	-0.002	f z(5z2-3r2)
f x(y2-z2)					-0.005	0.015		-0.011	0.003	-0.013	0.001	0.005	0.006	0.009	0.004	-0.002	-0.002	f x(y2-z2)
f y(z2-x2)								0.013	-0.013	-0.020	-0.001	-0.001	0.002	0.001	0.010	-0.010	-0.010	f y(z2-x2)
f z(x2-y2)					0.001	0.006		-0.005	0.001	-0.001	0.004	0.002	0.001	0.001	0.005	0.001	0.003	f z(x2-y2)
d 3z2-r2					-0.001	-0.006		-0.001	0.005	-0.001	0.002	0.004	0.001	-0.001	-0.005	-0.003	-0.001	d 3z2-r2
d x2-y2					-0.001	0.002		0.011	-0.006	-0.002	-0.001	-0.001	-0.038	0.014	-0.041	-0.023	-0.010	d x2-y2
d yz					0.001	-0.004		-0.009	-0.001	-0.001	0.001	0.014	-0.054	0.071	0.025	0.033	0.058	d yz
d zx					0.011	-0.004		-0.004	-0.004	-0.005	0.005	-0.041	0.071	0.026	-0.032	-0.032	0.134	d zx
d xy					-0.001	0.001		0.002	0.002	-0.010	-0.001	-0.023	0.025	-0.032	-0.053	0.001	0.028	d xy
s					-0.001	0.001		0.002	0.010	-0.003	0.001	-0.010	0.033	-0.032	0.001	-0.053	0.028	s
					0.006	0.001		-0.001	-0.001	-0.003	0.003	-0.033	0.058	-0.134	0.028	0.028	0.028	
	s	p x	p y	p z	f xyz	f x(5x2-3r2)	f y(5y2-3r2)	f z(5z2-3r2)	f x(y2-z2)	f y(z2-x2)	f z(x2-y2)	d 3z2-r2	d x2-y2	d yz	d zx	d xy	s	

no fitting!

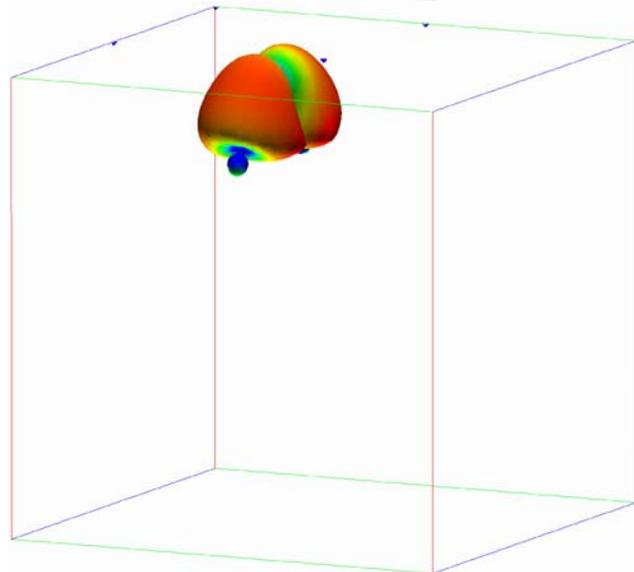
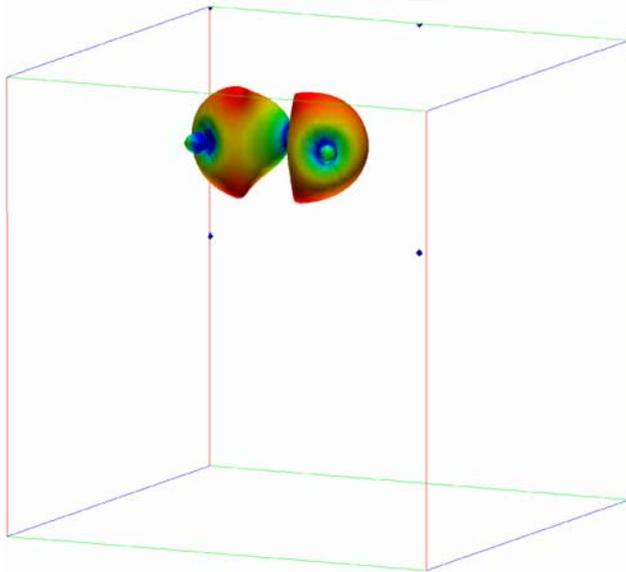
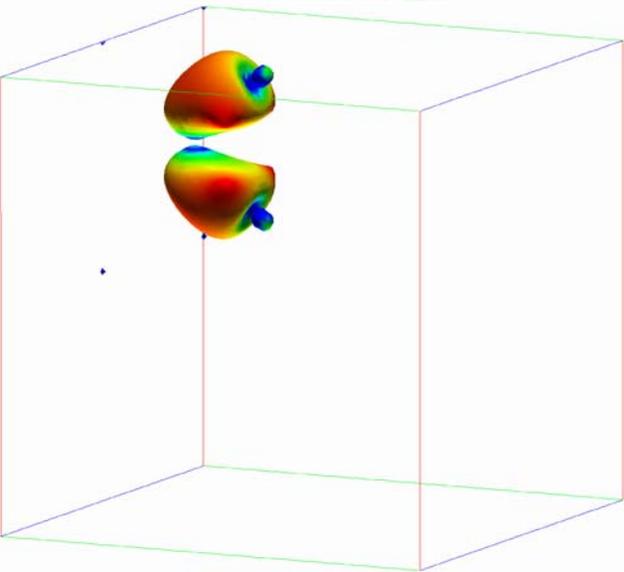
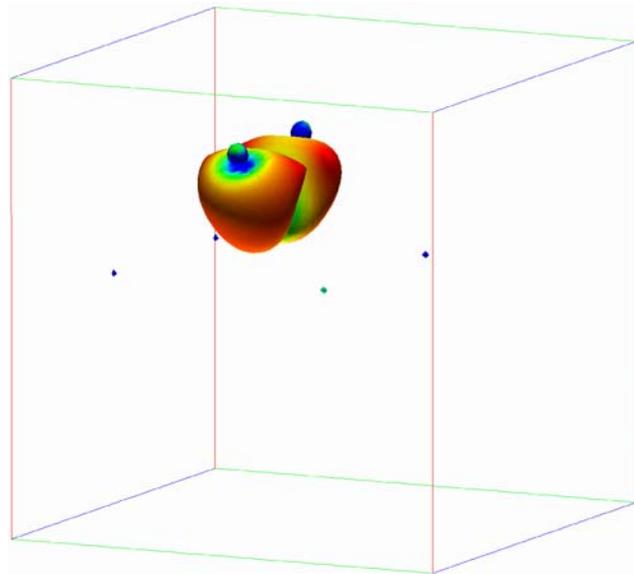
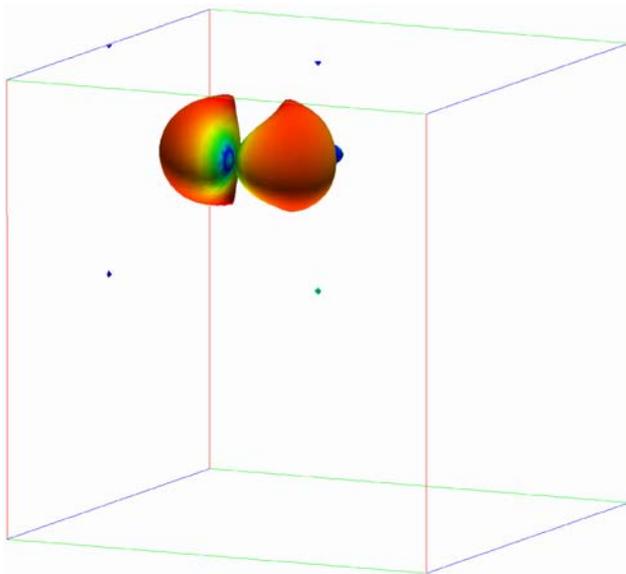
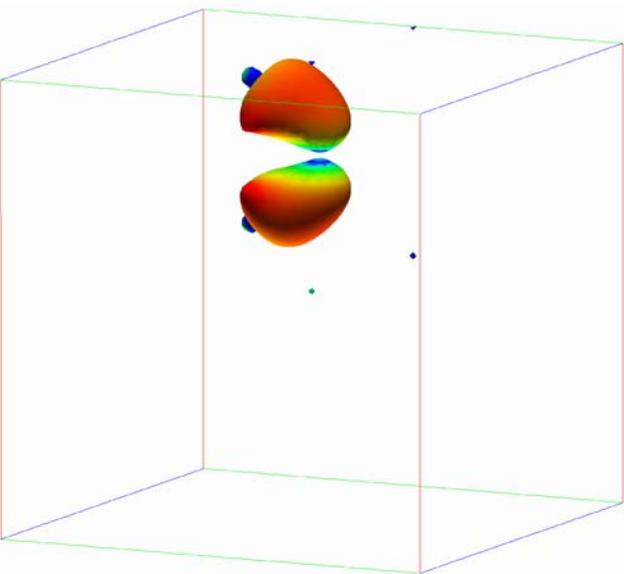
Bond-Centered WS – Si



Bond-Centered WS – CaB6

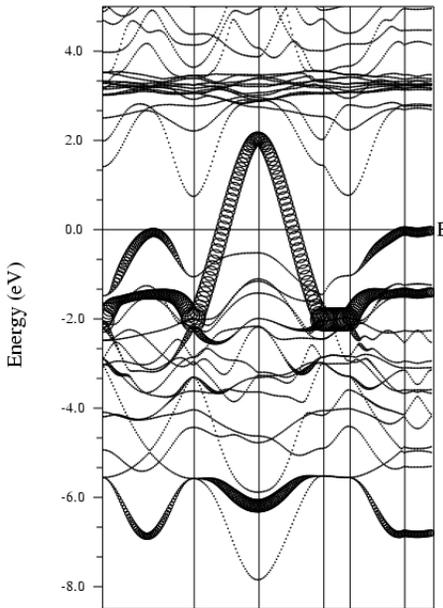


Non-Trivial Symmetry – CaB6

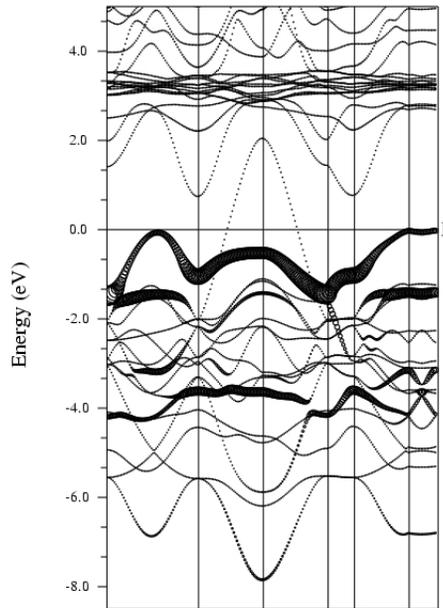


Bias for More Control – La_2CuO_4

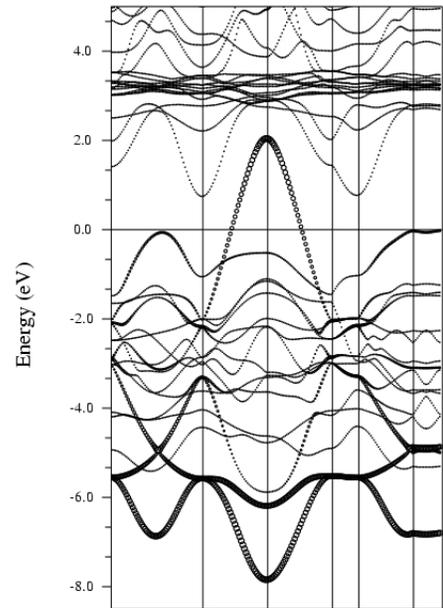
Cu – d x^2-y^2



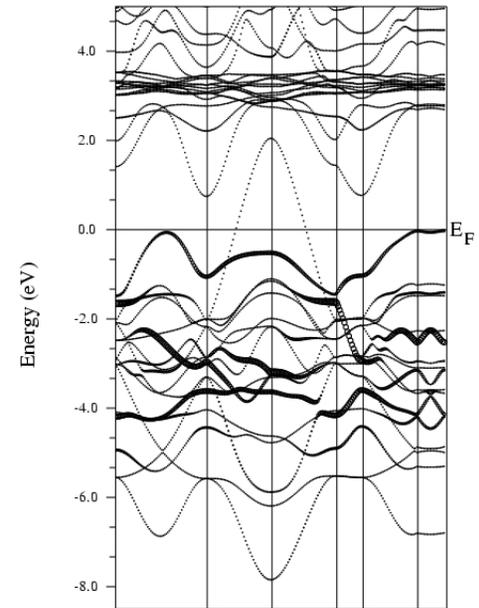
Cu – d z^2



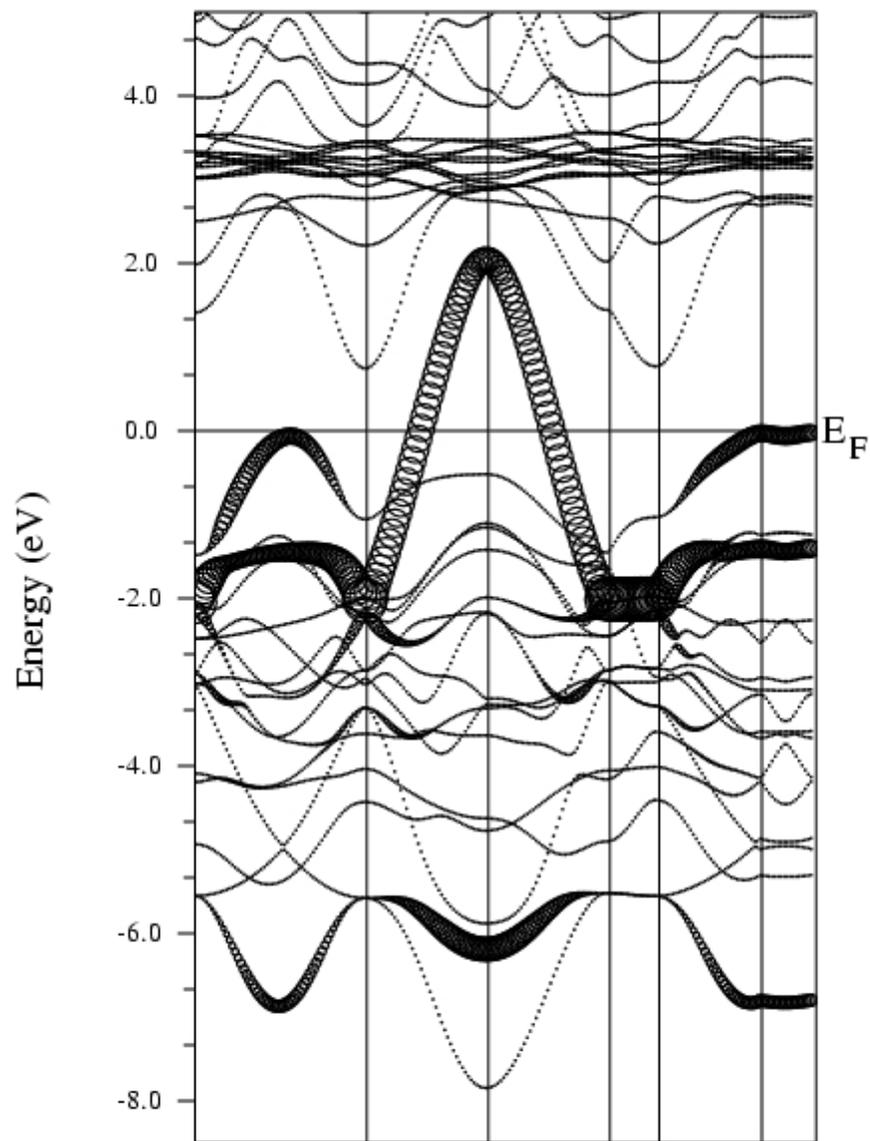
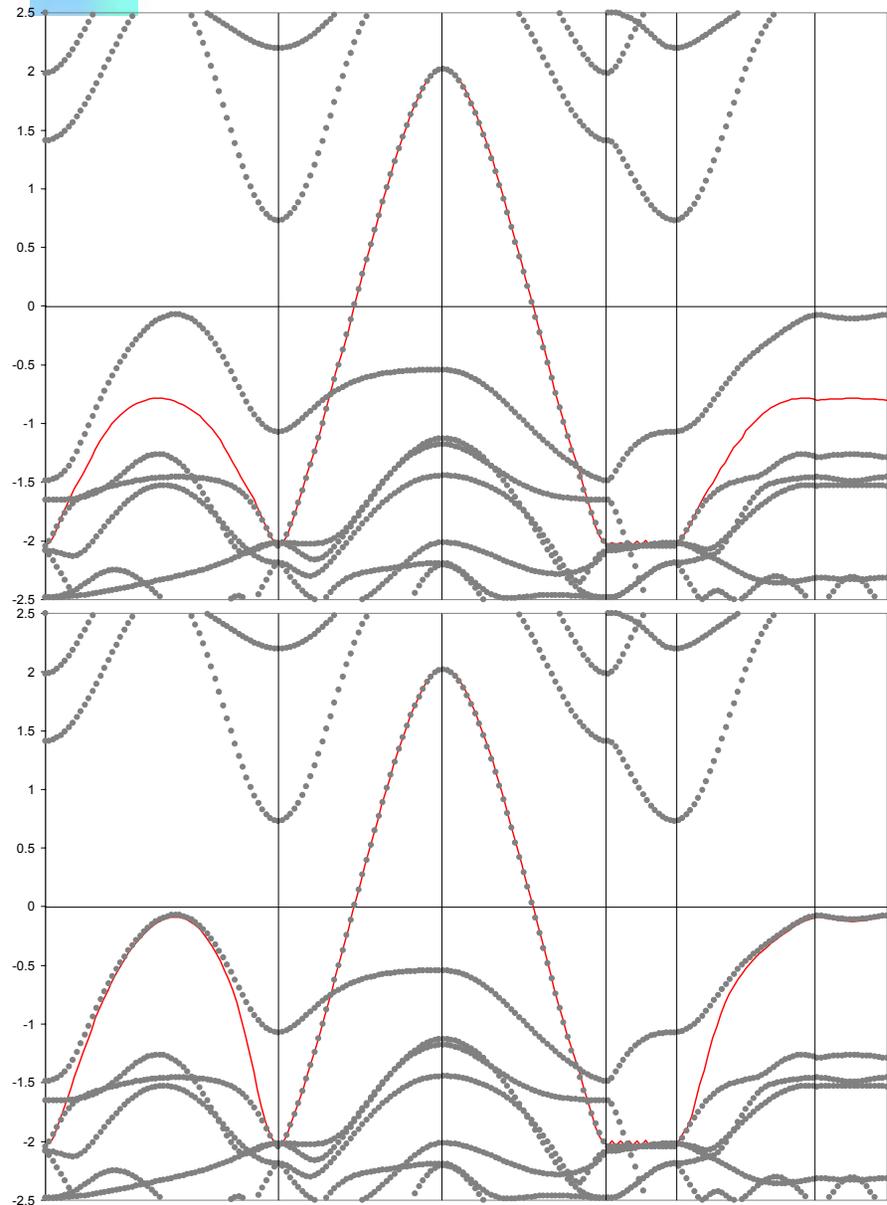
O1 – p y



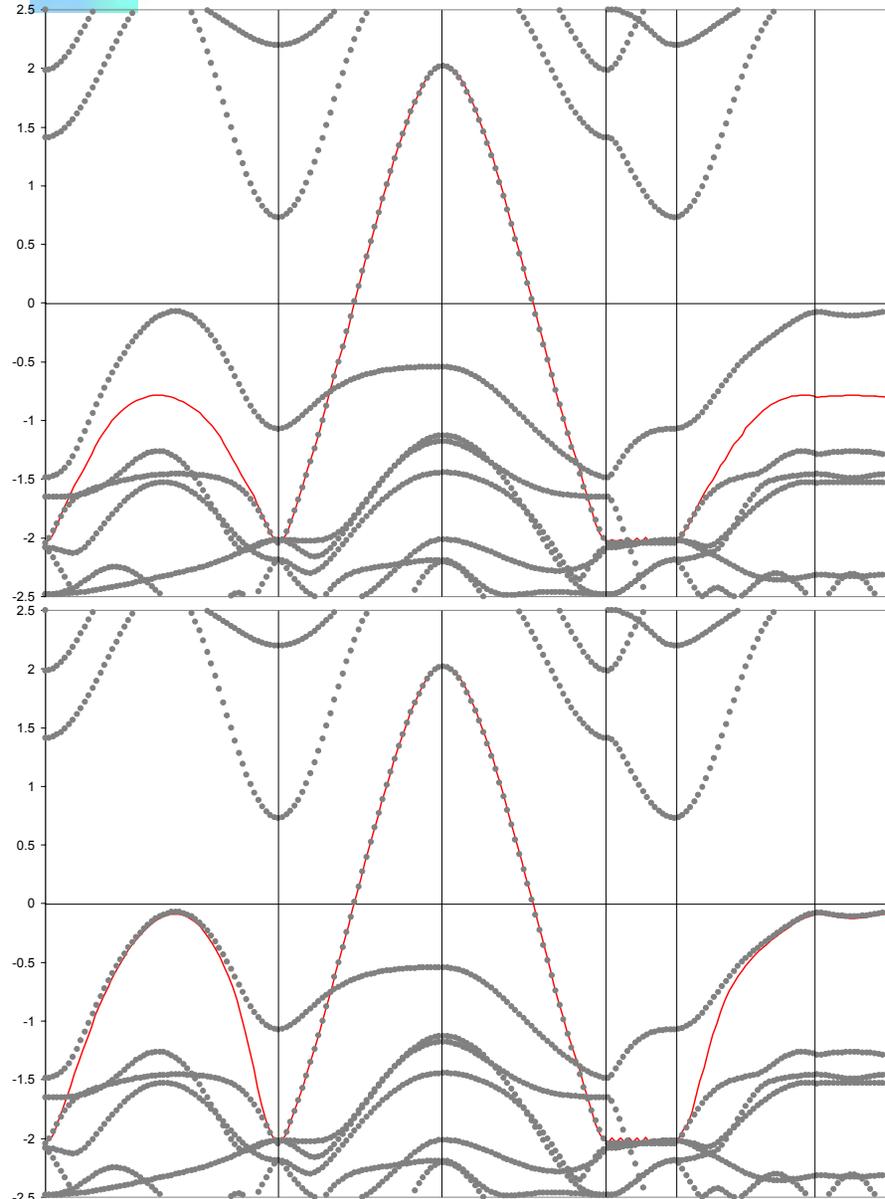
O2 – p z



Bias for More Control

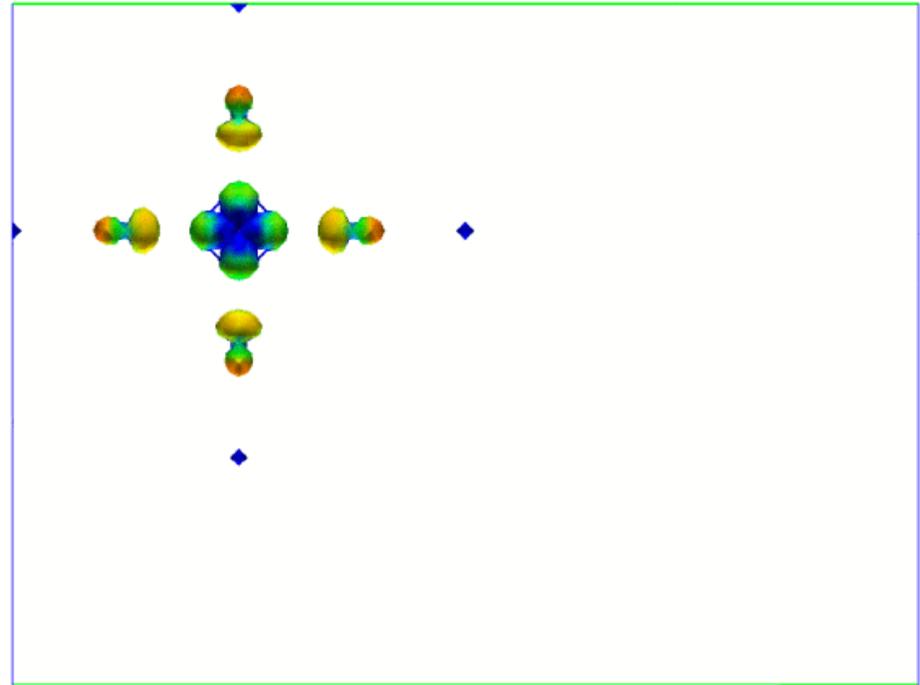
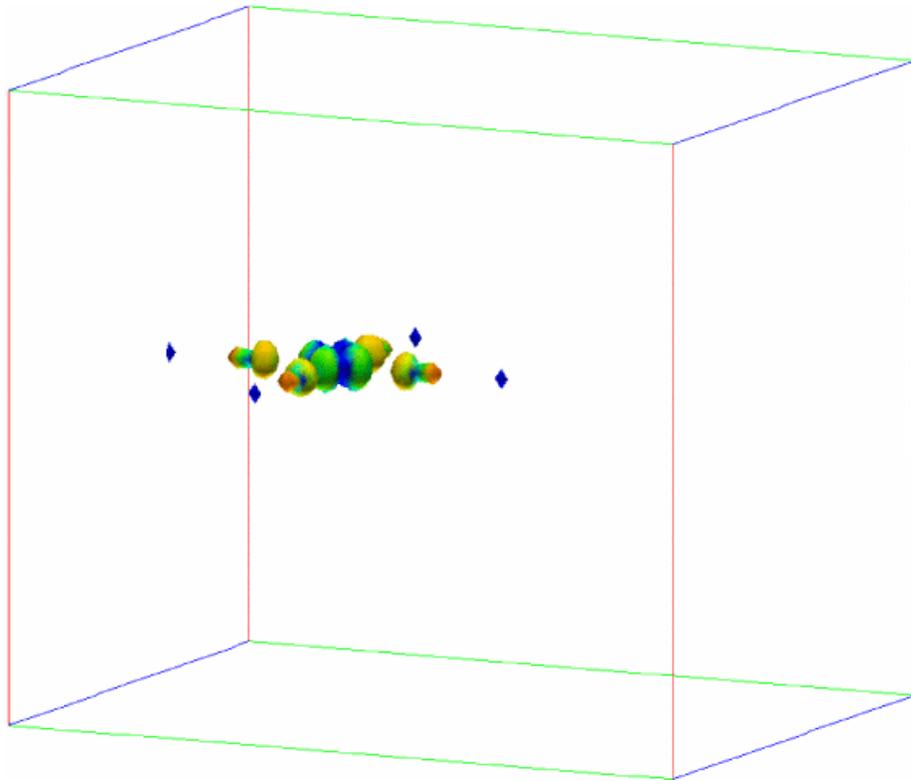


Bias for More Control



(alpha')	(meV)	(meV)
0 0 0	-85.3	94.5
0 1 0	-471.6	-430.0
-1 0 0	-471.6	-430.0
1 1 0	107.9	33.6
1 -1 0	107.9	33.6
0.5 0.5 0.5	2.9	-10.1
-0.5 -0.5 0.5	2.9	-10.1
0 2 0	-72.7	-30.8
-2 0 0	-72.7	-30.8
1 2 0	-0.7	-27.6
2 -1 0	-0.7	-27.6
0.5 1.5 0.5	-1.1	0.1
-1.5 -0.5 0.5	-1.1	0.1
1.5 1.5 0.5	-0.7	8.9
1.5 -1.5 0.5	-0.7	8.9
2 2 0	8.5	-1.0
2 -2 0	8.5	-1.0
0 3 0	-19.2	4.3
-3 0 0	-19.2	4.3

Half-Filled Wannier States of Cu-O in La_2CuO_4



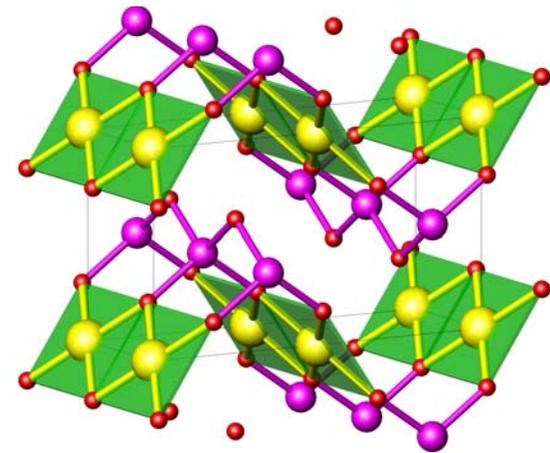
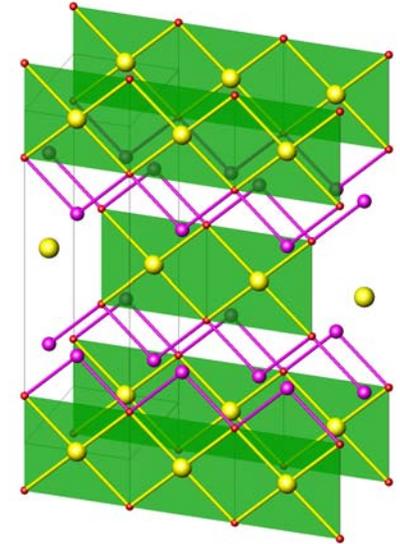
Rich Behavior of Quasi-1D Edge-Sharing Chains

- Large on-site repulsion
- Narrow bandwidth
- Half-filling
 - ~ Mott-Hubbard insulator
- Edge-sharing Cu-O chain
 - ~ 90° bond angle (94/99/94)

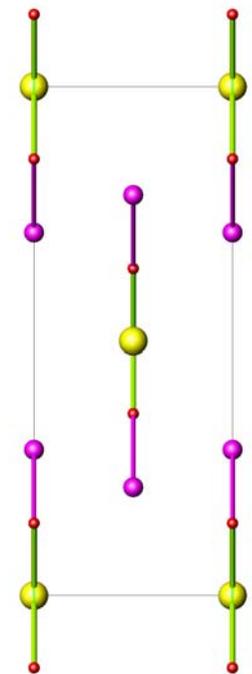
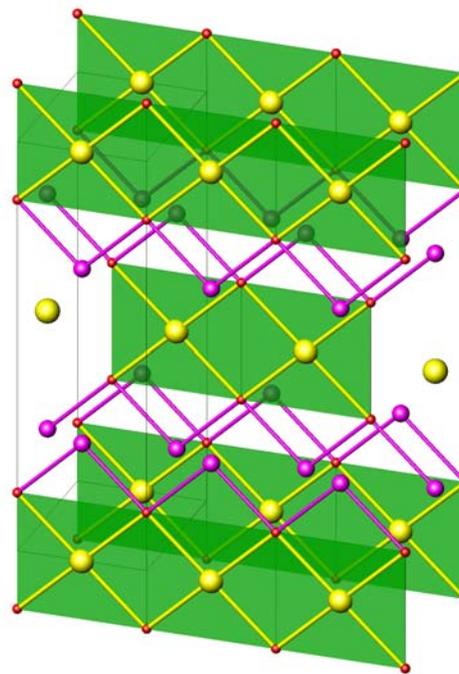
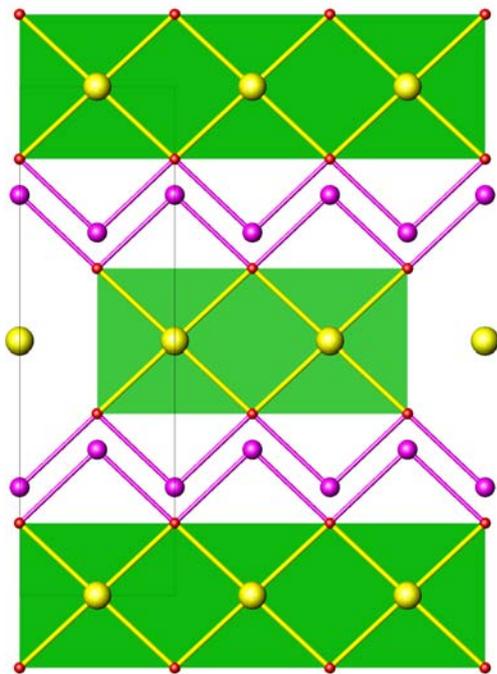
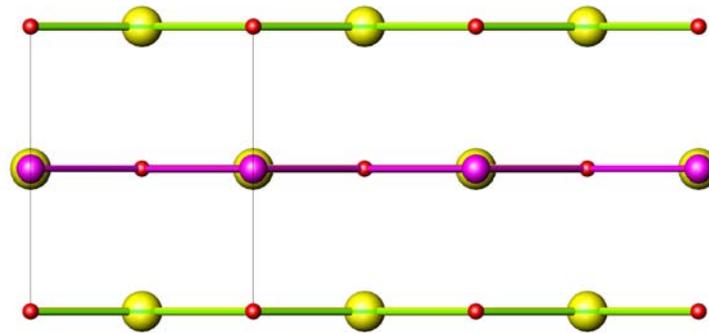
But different intra-chain order

- Li_2CuO_2 : ferromagnetic (FM) order
- CuGeO_3 : anti-ferromagnetic (AF) order
- CuSiO_3 : anti-ferromagnetic (AF) order

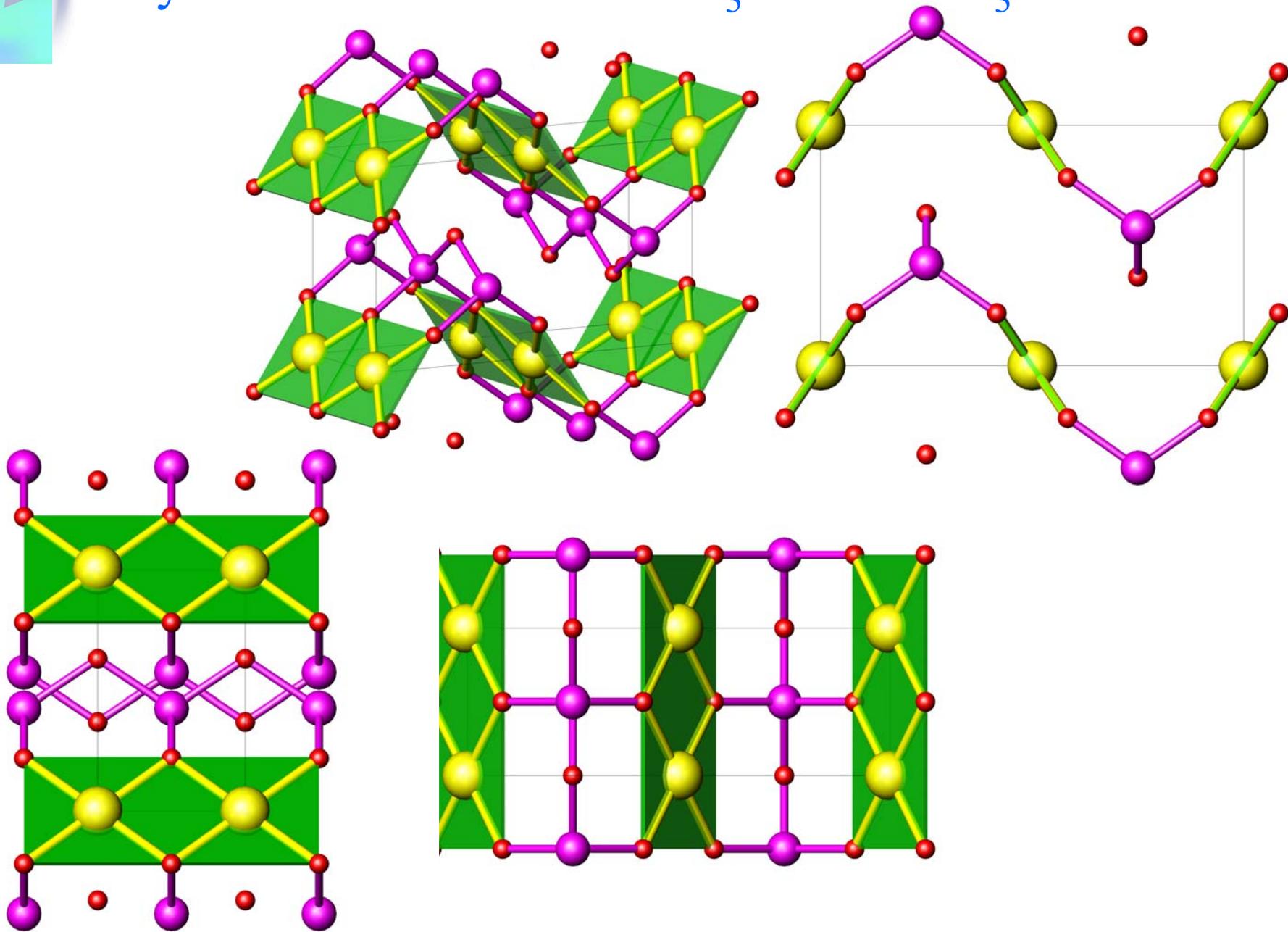
What is the underlying microscopic mechanism?



Crystal Structures of Li_2CuO_2



Crystal Structures of CuGeO_3 and CuSiO_3



How is the magnetic order determined theoretically?

- **Quick answer:**

Heisenberg Model:
$$H = -J \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j$$

- sign of J ?
- 2nd neighbor / inter-chain interaction ?

- ***Ab initio* answer:**

Energy Minimization: E_{FM}^{tot} vs. E_{AF}^{tot}

- quality of V_{xc} ?
- still a black box

- **Others...**

Intuitive insight + quantitative realism ?

Reformulation of *Ab Initio* 2nd-Quantized Hamiltonian

$$H = \varepsilon_{\bar{\mu}\bar{\alpha}} n_{\bar{\mu}\bar{\alpha}} - t_{\bar{\mu}\bar{\nu}} c_{\bar{\mu}\bar{\alpha}}^+ c_{\bar{\nu}\bar{\alpha}} + U_{\bar{\mu}} \tilde{n}_{\bar{\mu}\uparrow} \tilde{n}_{\bar{\mu}\downarrow} + \frac{1}{2} C_{\bar{\mu}\bar{\nu}} \tilde{n}_{\bar{\mu}\bar{\alpha}} \tilde{n}_{\bar{\nu}\bar{\beta}} - J_{\bar{\mu}\bar{\nu}} \left(\mathbf{S}_{\bar{\mu}} \cdot \mathbf{S}_{\bar{\nu}} + \frac{1}{4} n_{\bar{\mu}\bar{\alpha}} n_{\bar{\nu}\bar{\beta}} \right) \\ + \text{other } \left(c_{\bar{\mu}\bar{\alpha}}^+ c_{\bar{\mu}'\bar{\alpha}} \right) \left(c_{\bar{\nu}\bar{\beta}}^+ c_{\bar{\nu}'\bar{\beta}} \right) \text{ terms} + \text{constant terms}$$

$$\varepsilon_{\mu\alpha} \equiv \left\langle \mu \left| h^{DFT} - v^{xc} \right| \mu \right\rangle - U_{\mu} \left\langle n_{\mu\alpha} \right\rangle^{DFT}$$

$$t_{\mu\nu} \equiv - \left(\left\langle \mu \left| h^{DFT} - v^{xc} \right| \nu \right\rangle - J_{\mu\nu} \left\langle c_{\bar{\nu}\bar{\beta}}^+ c_{\mu\bar{\beta}} \right\rangle^{DFT} \right) (1 - \delta_{\mu\nu})$$

$$U_{\mu} \equiv \langle \mu\mu | v | \mu\mu \rangle; \quad C_{\mu\nu} \equiv \langle \mu\nu | v | \mu\nu \rangle (1 - \delta_{\mu\nu}); \quad J_{\mu\nu} \equiv \langle \mu\nu | v | \nu\mu \rangle (1 - \delta_{\mu\nu}) \quad \tilde{\delta} \equiv o - \langle o \rangle^{DFT}$$

- Explicitly utilizing solutions of DFT
- First-principles & double-counting free
- notice the direct exchange term
- Inclusion of long-range Coulomb repulsion $\rightarrow \tilde{n}_{\mu\alpha}$
- Self-interaction eliminated in $\varepsilon_{\mu\alpha}$
- Quality of h^{DFT} : LDA

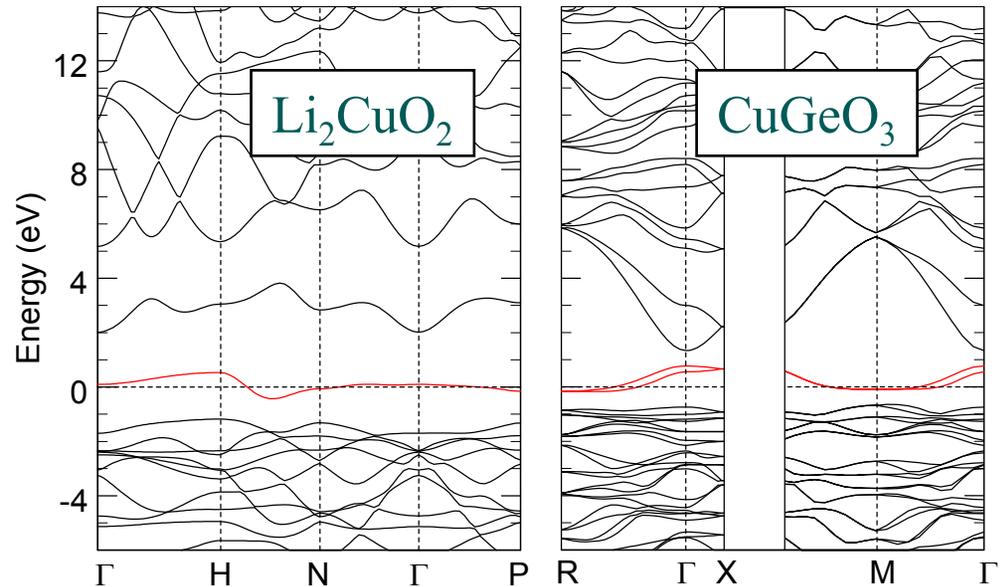
Wannier States as Basis

$$|Rn\rangle \equiv |\bar{k}n\rangle e^{-i\bar{k}\cdot R} / \sqrt{\#}$$

$$|kn\rangle = |\phi_{k\bar{m}}\rangle \langle \phi_{k\bar{m}} | kn \rangle$$

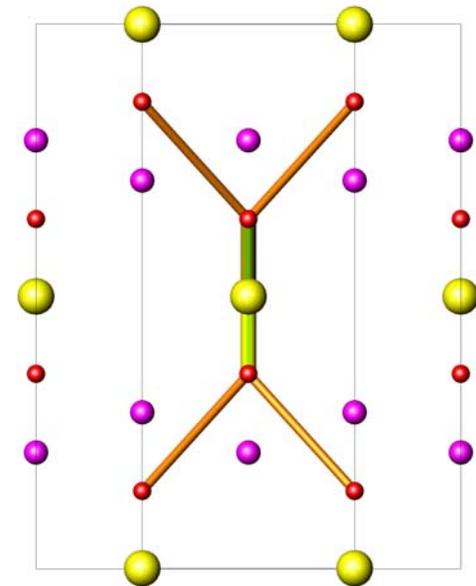
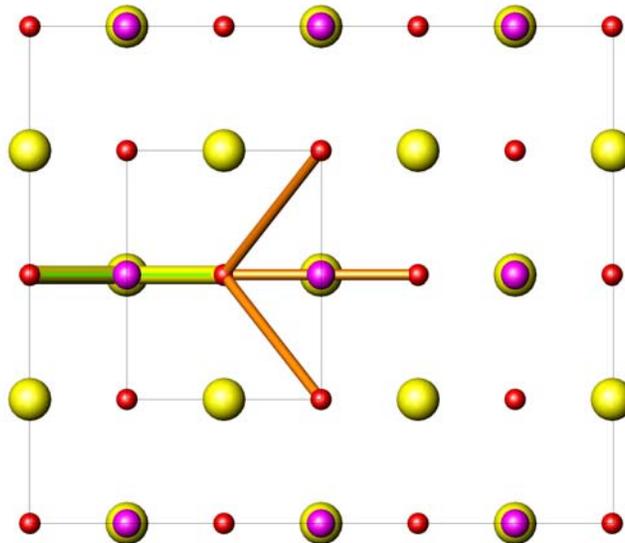
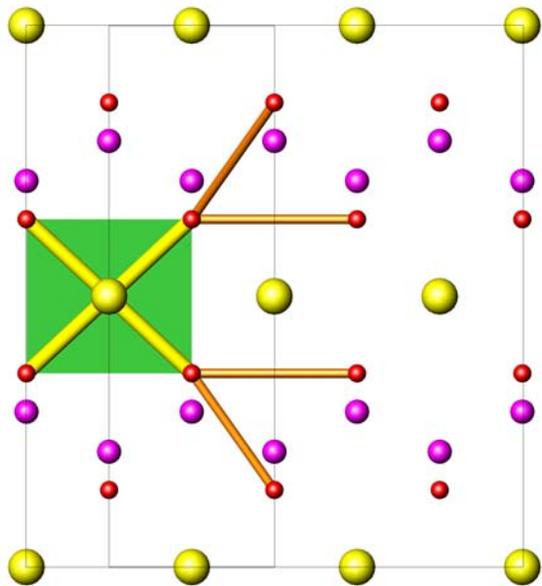
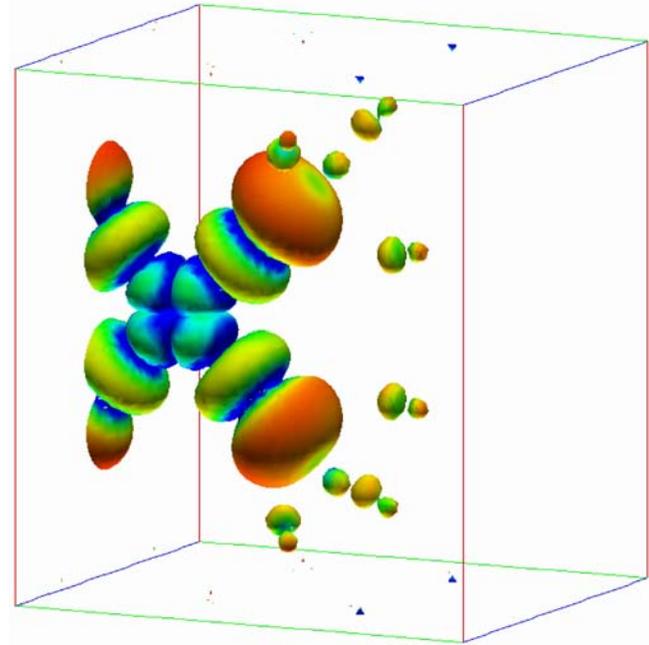
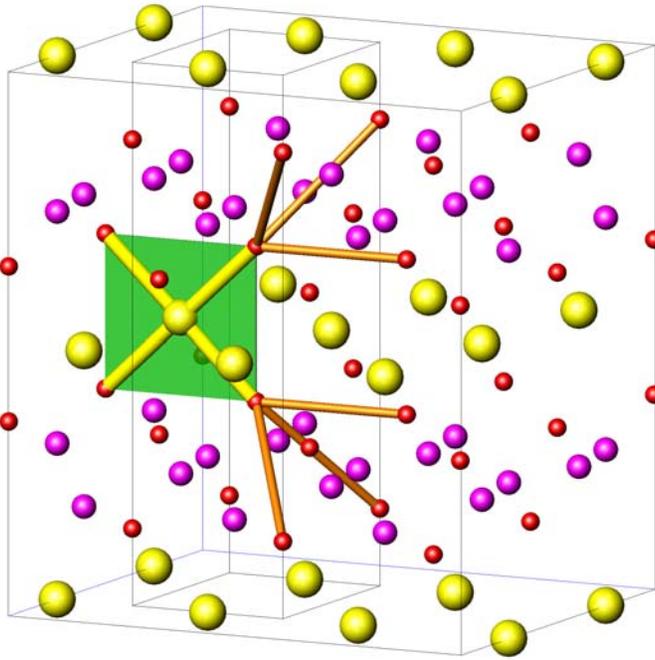
$$\langle \phi_{km} | kn \rangle = \langle \phi_{km} | g_{\bar{n}'} \rangle M_{\bar{n}'n}$$

$$M_{\bar{n}'n}^{-2} \equiv \langle g_{\bar{n}'} | \phi_{k\bar{m}} \rangle \langle \phi_{k\bar{m}} | g_n \rangle$$



- Localized picture (desired for spin analysis)
- Orthonormal + Complete (unlike atomic orbitals)
- Energy resolution (chosen band indices)
 - One per Cu site (two per unit cell) \rightarrow simpler picture
 - Half-filled
- Non-perturbative inclusion of hybridization
- All-electron wave function

Low-Energy Wannier States of Li_2CuO_2



Wannier representation of H and screening

- Partial spin density:

Cu : 50%, O : 4 x 10%

- $t_{ij} \sim -\langle i | h^{DFT} | j \rangle (1 - \delta_{ij})$ is *calculated*, not fitted.
(perfect “downfolding”)

- U_i and J_{ij} are evaluated via 6D numerical integration

- AF via superexchange (leading hopping paths)

$$\mathcal{J}_z^{SX} \sim \sum \mathcal{J}_{ij}^{SX} \sim \sum -4t_{ij}^2/W_i; \quad W_i \sim U_i/3$$

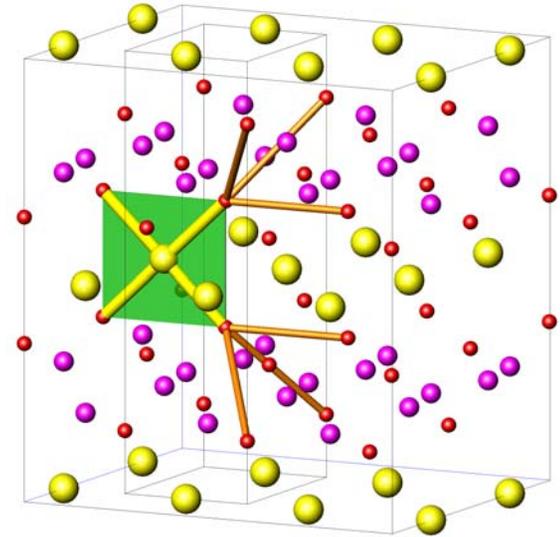
- FM via direct exchange

$$\mathcal{J}_z^{DX} \sim \sum J_{ij}^{SX} / 3$$

Calculated Parameters for Li_2CuO_2

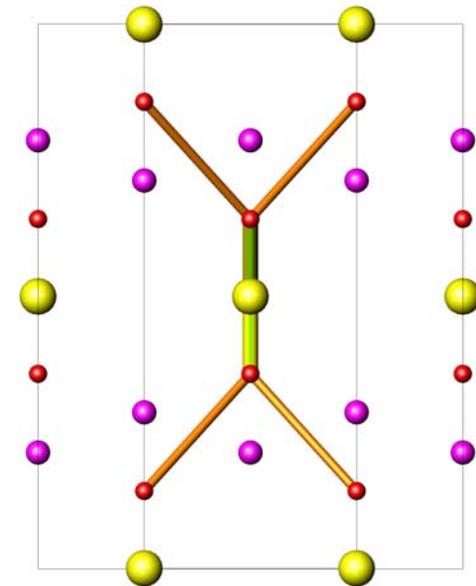
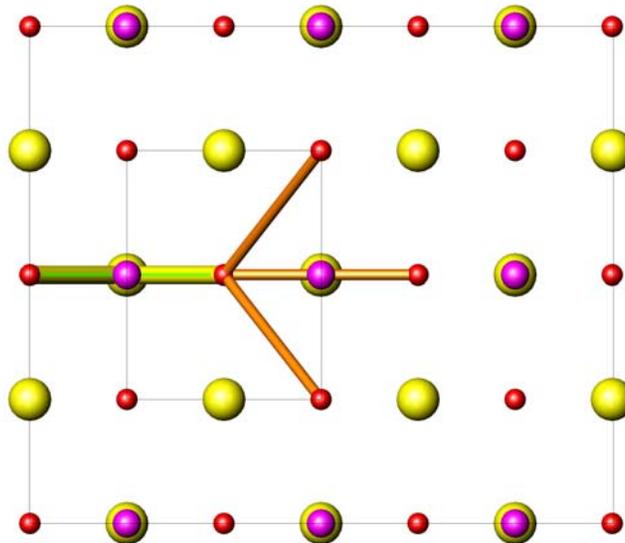
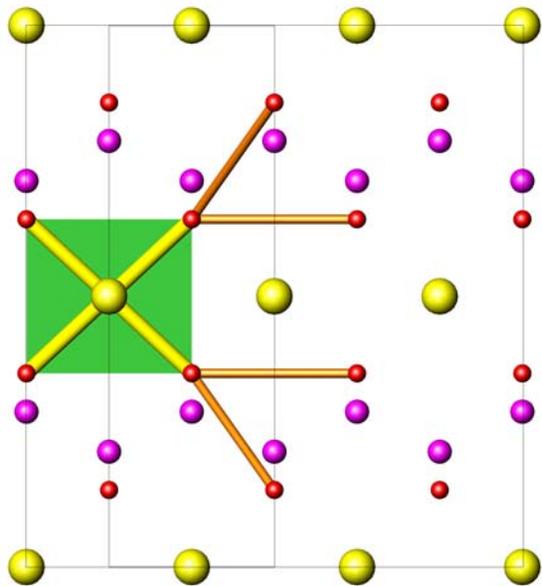
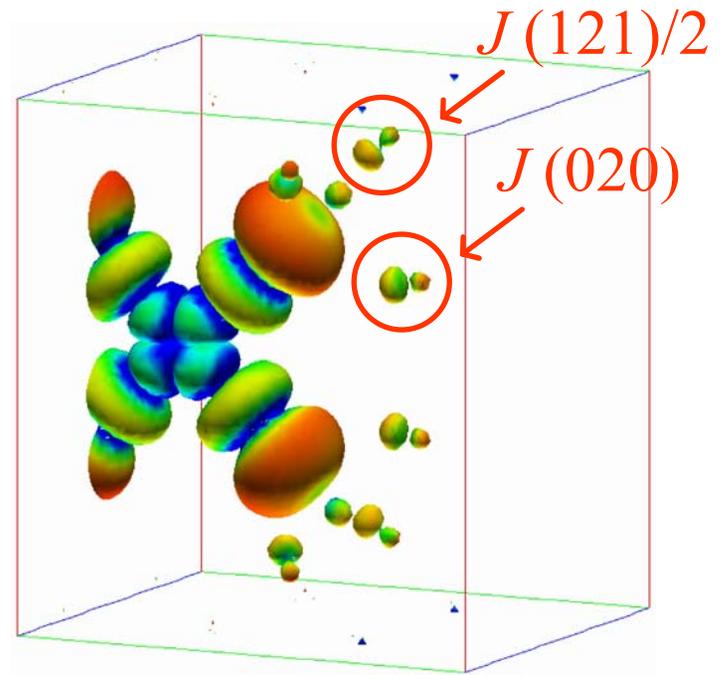
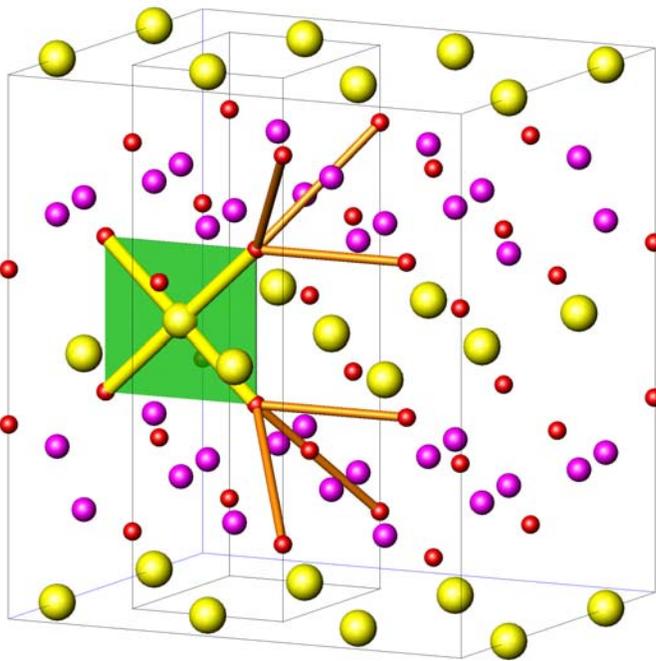
$i - j$	(010)	(020)	(030)	$U_i = 9.85 \text{ eV}$
t_{ij}	-66.7	-80.7	-19.2	$ \mathcal{J}_{\parallel}^{SX} = -5.9 $
J_{ij}	44.2	4.5	~ 0	$ \mathcal{J}_{\parallel}^{DX} = \wedge $

$i - j$	(111)/2	(131)/2	(100)	(001)	(meV)
t_{ij}	-17.2	41.4	7.2	1.9	$ \mathcal{J}_{\perp}^{SX} = -4.9 $
J_{ij}	1.5	3.6	~ 0	~ 0	$ \mathcal{J}_{\perp}^{DX} = \vee = +3.5 $

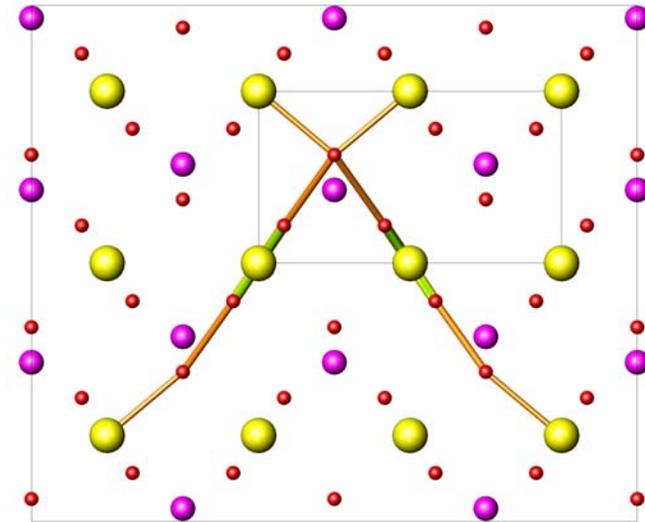
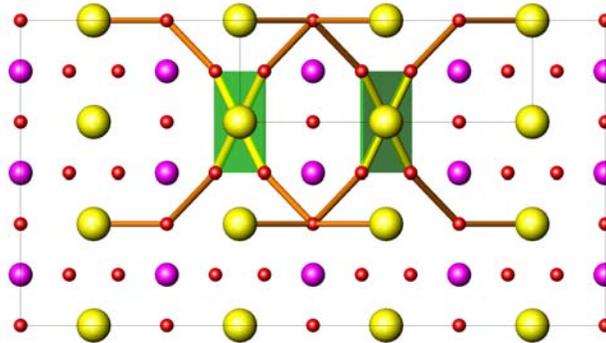
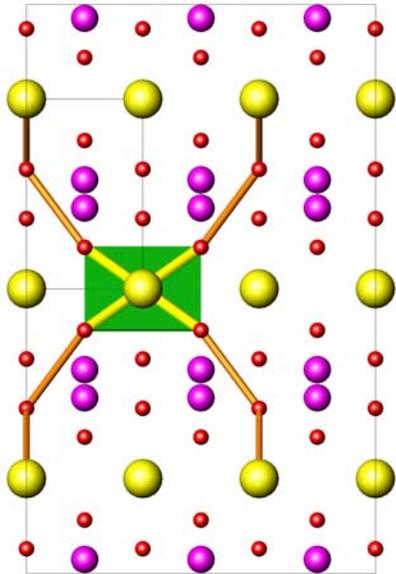
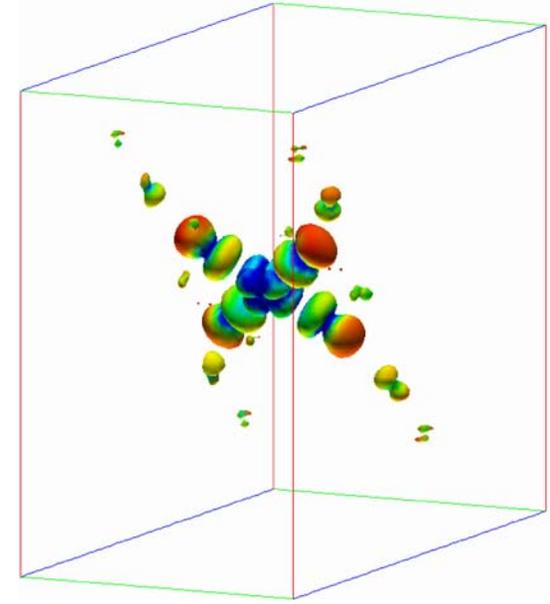
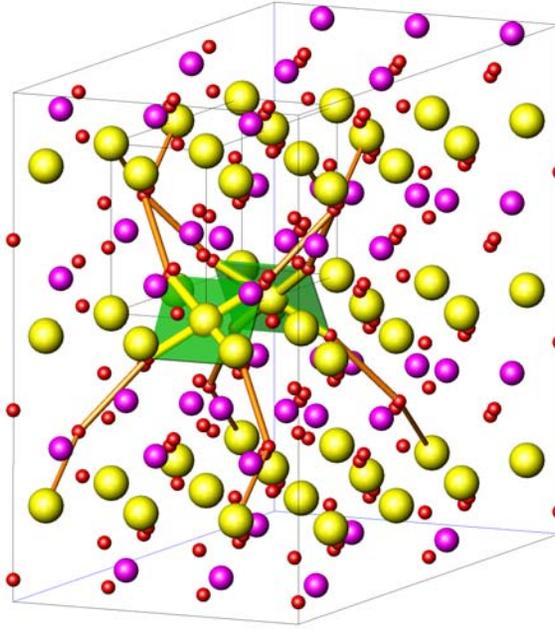
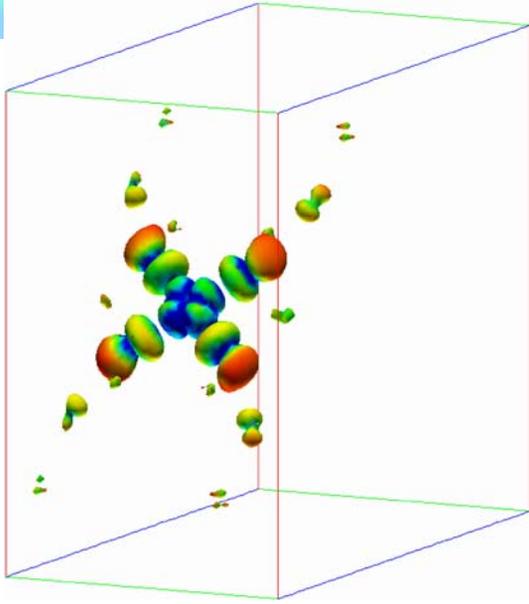


- Partial spin density: Cu: 50%, O: 4 x 10%
- “screening” parameter: 3
- 2nd NN hopping > 1st NN hopping
- sizeable inter-chain hopping
- intra-chain: **DX** overwhelms **SX** → **FM** couplings
- inter-chain: **SX** overcomes **DX** → **AFM** couplings

Observation of Hopping and Exchange



Low-Energy Wannier States of GuGeO_3



Calculated Parameters for GuGeO_3 (meV)

$i - j$	(010)	(020)
t_{ij}	-174.5	-68.4
J_{ij}	46.4	4.9

$$U_i = 11.3 \text{ eV}$$

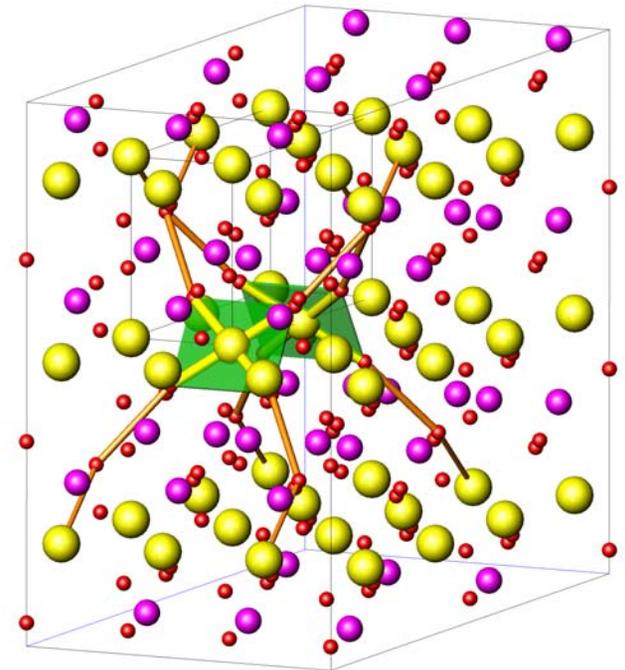
$\mathcal{J}_{\parallel}^{SX} = -32.4$	$\mathcal{J}'_{\parallel}{}^{SX} = -5.0$
$\mathcal{J}_{\parallel}^{DX} = +15.5$	$\mathcal{J}'_{\parallel}{}^{DX} = +1.6$

$i - j$	(100)	(110)	(120)
t_{ij}	-51.9	-16.2	10.2
J_{ij}	5.6	2.1	~ 0

$\mathcal{J}_x^{SX} = -2.9$
$\mathcal{J}_x^{DX} = +1.9$

$i - j$	(001)	(111)
t_{ij}	-14.1	-1.9
J_{ij}	1.8	6.4

$\mathcal{J}_z^{SX} = -0.2$
$\mathcal{J}_z^{DX} = +5.1$

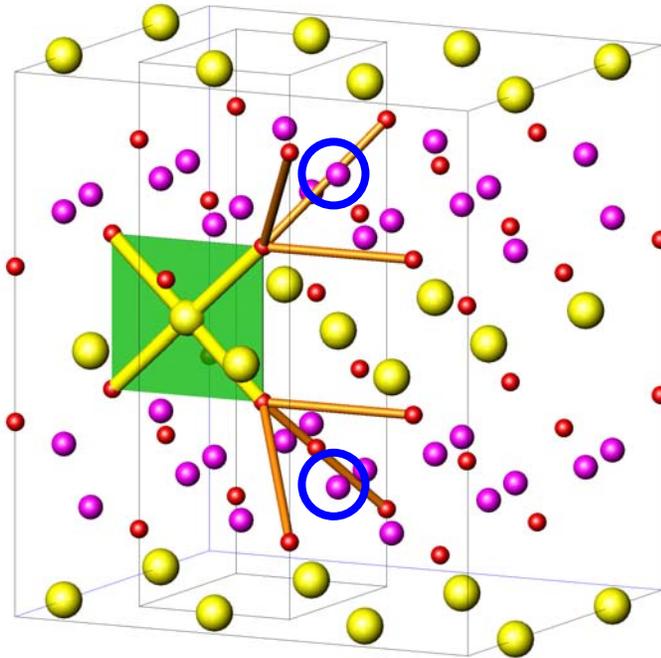


- **SX** overwhelms **DX**: intra- and inter-chain **AFM** couplings
- $\mathcal{J}'_{\parallel} / \mathcal{J}_{\parallel} \sim 1/5 \rightarrow$ spin-Peierls transition ?
- weak inter-plane hopping \rightarrow inter-chain **FM** couplings!

Effects of Crystal Field

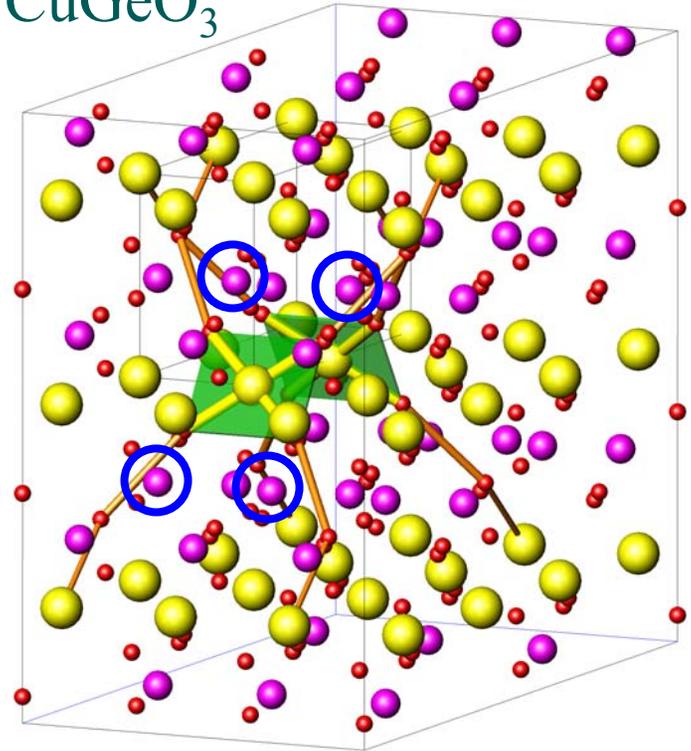
- direction of “growth” of the Wannier function!
- breaking the O- p y-z symmetry

Li_2CuO_2



- Dominant 2nd NN hopping
- 1st NN **DX** overwhelms **SX**
→ **FM** intra-chain
- 3D hopping → **AFM** inter-chain

CuGeO_3



- Dominant 1st NN hopping
→ **AFM** chain
- Sizeable 2nd NN hopping
- 2D hopping



Conclusion

- Novel *ab initio* scheme:
 - Reformulation of *ab initio* second-quantized H
 - Wannier state representation
 - Energy-resolved localized all-electron Wannier States
 - Intuitive microscopic picture + quantitative realism
- Unified picture of Insulating Magnetic order:
 - Ferromagnetism in Li_2CuO_2 :
 - Enhanced 2nd NN hopping
 - Strong intra-chain FM direct exchange at O
 - 3D hopping \rightarrow AFM inter-chain coupling
 - Anti-ferromagnetism in CuGeO_3 & CuSiO_3 :
 - Dominant AFM coupling from 1st NN hopping
 - Sizeable 2nd NN coupling \rightarrow spin-Peierls transition ?
 - Strong inter-plane FM direct exchange via Cu
- Important role of crystal field (in addition to the bond angle)



Future development: systems with stronger correlation one scenario within DOE-CMSN

DFT (SIC, LDA+U)

→ Bloch states & eigenenergies

- complete basis in large energy scale
- reasonable energy resolution
- proper hybridization



Wannier Construction

→ Wannier states

→ full lattice Hamiltonian

- multiple energy resolution
- localized basis
- non-perturbative inclusion of hybridization



QMC, FLEX, DMFA, DCA

→ physical observables

- careful treatment of quantum correlation
- dynamical excitation spectrum
- long range order
- phase transition
- volume collapse



Numerical Canonical Transformation

→ reduced effective Hamiltonian

- numerical renormalization group
- effective inclusion of high-energy excitation
- 1st-principles derivation of few-band “model”